CONTENTS.

'APERS COMMUNICATED TO THE CHEMICAL SOCIETY.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS:—

PART I.

Organic Chemistry.

Physiological Chemistry.

Chemistry of Vegetable Physiology and Agriculture.

PART II.

General and Physical Chemistry.

Inorganic Chemistry.

INDEX OF AUTHORS' NAMES

IN TRANSACTIONS AND ABSTRACTS

C.

D.

E.

H.

I.

J.

K.

N.

O.

P.

R.

S.

ERRATA.

Vol. CIII (Trans., 1913).

Page.	Line.				
1613	16*	*for*	"$\begin{array}{c}C_6H_5\cdot C\\ \|\\ N\cdot OH\end{array}$"	*read*	"$\begin{array}{c}C_6H_5\cdot CH\\ \|\\ N\cdot OH\end{array}$"
1624	6	,,	"tube to 100°"	,,	"tube with benzene to 100°."

Vol. CIV (Abstr., 1913).

Page.	Line.				
i, 1138	25 } 17* }	*for*	"Gilman"	*read*	"Gilmour."
ii, 546	21*	,,	"**Albumin**"	,,	"**Aluminium**"
ii, 621	15*	,,	"690—691"	,,	"677—679, 690—691."

* From bottom.

me cases the density was determined by weighing a brass (1) in air, (2) in water at a known temperature, (3) sus- in the fused substance at the temperature of its melting

ıe other cases the density was determined by drawing the ubstance up into a pipette (previously calibrated by weigh- h mercury) aud then weighing.

tance.	Temper-ature.	Density.		Temper-ature.	Specific volume.	Molecular volume.
benzene......	131°	1·1195	—	—	0·89325	164·4
uiline	36	1·0586	1·0700	33°	0·94461	172·9
deneaniline ..	50	1·0450	1·0739	49	0·95691	173·3
zene	67	1·0498	1·0901	69	0·95258	173·8
l	52	0·9682	1·014	52	1·0328	188·0
....	125	0·9544	0·9707	124	1·0478	188·6
....	94	1·1036	—	—	0·90608	190·2
....	134	1·0790	—	—	0·92680	196·1
lide	161	0·9161	—	—	1·0916	215·2
enzoin...	134	0·9271		—	1·0786	230·8

will be observed that there are two values given for the ity of some of the substances in the above table.

ıe second values are those obtained by Beck (*Zeitsch. physikal. m.*, 1904, **48**, 657); they differ considerably from the values obtained.

eck used the method of balancing columns of liquid in a U-tube ch would fail to give accurate results.

Hydrazobenzene has a much lower molecular volume than the er substances in this series. It is worthy of notice that Beck nd that the viscosities of these substances at their melting nts were approximately constant (2·5) with the exception of drazobenzene, which had the value 2·918 (*loc. cit.*).

The substances with the greatest molecular volumes are those ich contain an oxygen atom, namely, benzil, benzoin, benzanilide, d hydrobenzoin, and it is concluded that the molecular domains these substances are greater than those of the other substances, d consequently they show more limited miscibility in the solid ıte. It will be observed also that the molecular volume of a turated substance at its melting point is less than that of the turated substance.

This rule has been observed previously for substances at the perature of their boiling points (Buff, *Annalen Suppl.*, 1865, 129; Schiff, *Annalen*, 1883, **220**, 301).

Further discussion of the miscibility of substances of the type aβPh is postponed until a larger number of binary mixtures has n examined.

Summary.

(1) Binary mixtures of benzoin with compounds of the type Ph$\alpha\beta$Ph give thermal diagrams having a single eutectic point, and forming two series of solid solutions.

The miscibility is limited—never complete.

(2) Binary mixtures of benzil with compounds of the type Ph$\alpha\alpha$Ph and Ph$\alpha\beta$Ph behave similarly.

(3) The position of the eutectic point (temperature and concentration) depends on the melting points of the substances. The eutectic mixture always contains a larger percentage of the constituent of lower melting point.

(4) It is suggested that the CO and CH(OH) groupings give a greater spatial domain to the molecules, and that this accounts for the more limited miscibility of benzil than of other compounds of the type Ph$\alpha\alpha$Ph.

CHEMICAL LABORATORY, THE UNIVERSITY,
EDGBASTON, BIRMINGHAM.

CXCIX.—*Coumaranone Derivatives. Part II. The Constitution of Ethyl Coumaranonecarboxylate.*

By RICHARD WILLIAM MERRIMAN.

SEVERAL distinct observations indicate that ethyl coumaranonecarboxylate normally exists in the enolic form (I):

$$C_6H_4\left<\begin{matrix}O\\C(OH)\end{matrix}\right>C\cdot CO_2Et \qquad\qquad C_6H_4\left<\begin{matrix}O\\C(:N\cdot NHPh)\end{matrix}\right>CH\cdot CO_2Et$$

(I.) (II.)

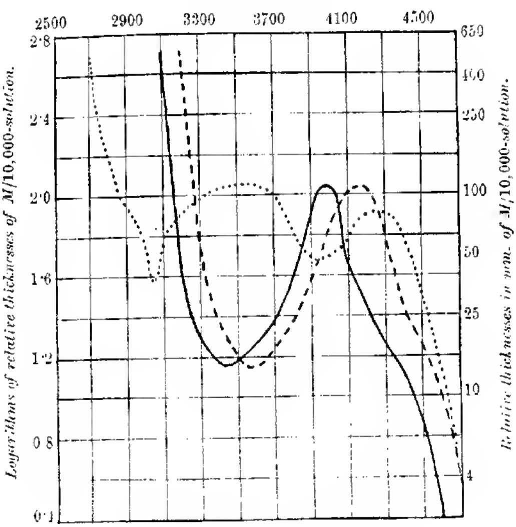
(*a*) Out of fifty attempts to prepare the phenylhydrazone (II), described in Part I. (T., 1911, **99**, 911), by the interaction of an alcoholic solution of the ester and a solution of phenylhydrazine in 50 per cent. acetic acid, only two were successful. In all the other cases, when air was excluded an isomeric substance with entirely different properties was formed. The phenylhydrazone melts at 126°, and undergoes normal hydrolysis with alkalis and acids, and its behaviour towards light is similar to that of benzaldehydephenylhydrazone. The isomeric substance melts at 142°, is not acted on by light, and is entirely stable towards all kinds of hydrolytic agents. It is probably the phenylhydrazino-derivative,

$$C_6H_4\left<\begin{matrix}O\\C(NH\cdot NHPh)\end{matrix}\right>C\cdot CO_2Et,$$

oduced from the enolic form of ethyl coumaranonecarboxylate.) All attempts to prepare the oxime of ethyl coumaranonecarb- ylate were unsuccessful. (*c*) The ester is strongly acidic. On rating its dilute alcoholic solution with $N/10$-sodium hydroxide, ing phenolphthalein as indicator, exactly one equivalent of the kali was required for neutralisation. (*d*) It reacts towards agnesium methiodide entirely in the enolic form. (*e*) Further idence for the enolic constitution of ethyl coumaranonecarb-

FIG. 1.

Oscillation frequencies.



——— *Ethyl coumaranonecarboxylate in alcohol.*
- - *Acetyl derivative.*
.... *Sodium derivative in water.*

xylate was obtained by comparing its absorption curve with that of its acetate. The curves are drawn in Fig. 1. The curve of the ester shows a deep band in the ultraviolet with its head at $1/\lambda$ 3440. The absorption curve of the acetyl derivative is parallel to the former curve throughout its length, with a slight shift towards the more refrangible end of the spectrum, the head of the band being at $1/\lambda$ 3560. The constitutions of the ester and its acetyl derivative are evidently identical, so that, assuming the ordinary formula for

acetyl compounds, the ester exists in the enolic form. Three different constitutions for the sodium derivative are possible:

$$C_6H_4<\overset{\text{——O——}}{C(ONa)}>C\cdot CO_2Et \qquad C_6H_4<{}^{O}_{CO}>CNa\cdot CO_2Et$$

(I.) (II.)

$$C_6H_4<{}^{O}_{CO}>C:C<{}^{ONa}_{OEt}.$$

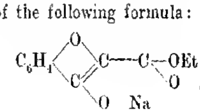
(III.)

Formula (II) would not account for the intense and characteristic colour of the ferric derivative. Formula (I) receives support from the work of Auwers (*Annalen*, 1912, **393**, 338). By the action of methyl sulphate and aqueous alkali at 0° on ethyl coumaranonecarboxylate, this author obtained the *O*-methyl ether,

$$C_6H_4<\overset{\text{——O——}}{C(OMe)}>C\cdot CO_2Et,$$

its formation being attributed to the action of the ions of the methyl sulphate on the ions of the sodium derivative of the strongly acidic ester.

The absorption curve of the sodium derivative, also given in Fig. 1, is entirely different from the other two curves. The solution used was made by dissolving the ester in the exact quantity of dilute aqueous sodium hydroxide required for neutralisation. The general absorption for the large thicknesses of solution is moved towards the visible spectrum in the usual manner. The band present in the absorption curves of the ester and of its acetyl derivative becomes narrower and less persistent, whilst its head is shifted to $1/\lambda$ 3050. A new band of small persistency, with its head at $1/\lambda$ 3930, also appears. A similar difference in the absorption spectra of an acetyl and a sodium derivative has been observed by Hantzsch (*Annalen*, 1912, **393**, 286) in the case of the 2-alkylindandiones. The stable sodium salt of ethyl coumaranonecarboxylate is probably considerably ionised, so that its constitution may be expressed according to the modification of Hantzsch's theory proposed by Brannigan, Macbeth, and Stewart (this vol., p. 415) by means of the following formula:



Other coumaranone derivatives react in the enolic form. For instance, Feuerstein and Brass (*Ber.*, 1904, **37**, 817) found that dihydroxycoumaranone, $C_6H_2(OH)_2<\overset{\text{——O——}}{C(OH)}>CH$, did not form an oxime or a phenylhydrazone.

Attempts to prepare the amide, $C_6H_4<{}^{O}_{CO}>CH\cdot CO\cdot NH_2$, by the action of alcoholic ammonia on ethyl coumaranonecarboxylate, always resulted in the formation of the ammonium salt of the ester, as was to be expected from the stability of the ester towards alkalis. The stability of ethyl coumaranonecarboxylate towards boiling alkalis is probably due to the salt formation, as Auwers (*loc. cit.*) found that the *O*- and *C*-alkyl derivatives were readily hydrolysed.

The monoamide of ethyl *o*-carboxyphenoxyacetate, previously described (Part I., T., 1911, **99**, 912), must have one of the following formulæ:

$$\underset{(I.)}{CO_2Et\cdot C_6H_4\cdot O\cdot CH_2\cdot CO\cdot NH_2} \quad \text{or} \quad \underset{(II.)}{NH_2\cdot CO\cdot C_6H_4\cdot O\cdot CH_2\cdot CO_2Et}.$$

If formula (I) is correct, the monoamide should react with metallic sodium in benzene solution in the same way as ethyl *o*-carboxyphenoxyacetate, with the formation of the amide of coumaranonecarboxylic acid:

$$C_6H_4<{}^{O\cdot CH_2\cdot CO\cdot NH_2}_{CO_2Et} + Na = H + EtOH + C_6H_4<{}^{O}_{CO}>CH\cdot CO\cdot NH_2.$$

On isolating the product from the sodium salt, however, it was found to be a new amic acid with the composition $C_9H_9O_4N$. Therefore the constitution of the monoamide of ethyl *o*-carboxyphenoxyacetate probably corresponds with formula (II), so that the amic acid (*o*-carbamylphenoxyacetic acid) has the formula:

$$NH_2\cdot CO\cdot C_6H_4\cdot O\cdot CH_2\cdot CO_2H.$$

Both the original monoamide and the amic acid gave, on hydrolysis, *o*-carboxyphenoxyacetic acid, which was first prepared by Rössing (*Ber.*, 1884, **17**, 2995). The formation of the amic acid from its ester is interesting, and the method might be capable of general application. The absorption curves of the amic acid and of its ester are given in Fig. 2. They are nearly parallel to each other throughout, and the head of the band is at $1/\lambda$ 3440 in each case. A comparison of these curves with that of ethyl coumaranonecarboxylate, given in the same figure, is not without interest. The three curves are as nearly as possible parallel with each other; the head of each band is at $1/\lambda$ 3440; the three bands are of exactly the same persistence. It seems that the band might be due to the same centre of vibration in each case, the intensity being much increased in the case of ethyl coumaranonecarboxylate owing to the formation of a carbonyl group in place of a carboxyl group. The equal persistence of the three bands is certainly curious, and points to the fact that the persistence of selective absorption bands is not without physical significance (compare Dawson, this vol., p. 1311).

Experimental.

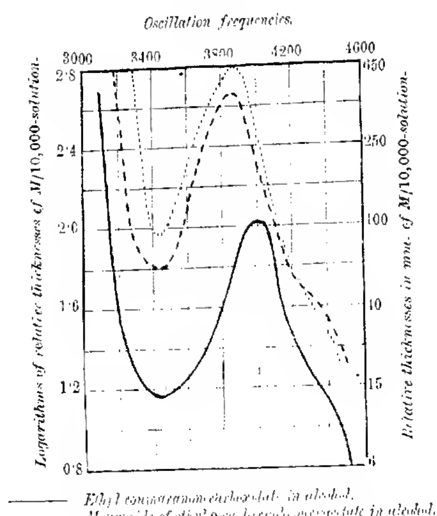
Ethyl Phenylhydrazinocoumaranonecarboxylate,

$$C_6H_4<\begin{matrix}-O-\\ C(NH\cdot NHPh)\end{matrix}>C\cdot CO_2Et.$$

This substance was obtained during most of the attempts to prepare the phenylhydrazone of ethyl coumaranonecarboxylate.

Phenylhydrazine (1 mol.) dissolved in 50 per cent. acetic acid was mixed with an alcoholic solution of ethyl coumaranonecarboxylate (1 mol.) contained in a tightly-stoppered flask filled with

Fig. 2.



hydrogen. In the course of two days yellow crystals separated, which, when recrystallised by dissolving in acetone and adding light petroleum, were obtained in yellow leaflets melting at 142°.

This substance is insoluble in alkalis or acids, and is not hydrolysed by them even on boiling for a long time:

0·1086 gave 0·2744 CO_2 and 0·0525 H_2O. C=68·9; H=5·4.
0·2057 „ 16·8 c.c. N_2 (moist) at 14° and 763 mm. N=9·7.
$C_{17}H_{16}O_3N_2$ requires C=68·9; H=5·4; N=9·5 per cent.

Titration of Ethyl Coumaranonecarboxylate,

$$C_6H_4<\overset{-O-}{C(OH)}>C\cdot CO_2Et.$$

The strongly acidic character of this ester was proved by titrating its solution in dilute alcohol with $N/10$-sodium hydroxide, using phenolphthalein as indicator:

0·2376 gram neutralised 11·6 c.c. $N/10$-NaOH. Equivalent weight = 205.

$C_{11}H_{10}O_4$ requires equivalent weight = 206.

Ethyl Acetocoumaranonecarboxylate,

$$C_6H_4<\overset{-O-}{C(OAc)}>C\cdot CO_2Et.$$

Ethyl coumaranonecarboxylate (3 grams) was heated with acetic anhydride (10 grams) and fused sodium acetate (3 grams) for two hours. The hot mixture was poured into hot alcohol to remove the excess of acetic anhydride. The acetyl compound, after crystallisation from dilute alcohol, separated, like the parent ester, as an emulsion, which changed into long, white needles, melting at 77°:

0·1937 gave 0·4463 CO_2 and 0·0861 H_2O. C = 62·9; H = 4·95.

$C_{13}H_{12}O_5$ requires C = 63·0; H = 4·85 per cent.

This acetyl derivative is stable towards cold alkalis.

Ethyl Benzocoumaranonecarboxylate,

$$C_6H_4<\overset{-O-}{C(OBz)}>C\cdot CO_2Et.$$

Ethyl coumaranonecarboxylate was boiled for three hours with sodium benzoate and benzoyl chloride, the product being worked up in the usual way. *Ethyl benzocoumaranonecarboxylate* crystallises from light petroleum in glistening, white needles, melting at 123°, and is readily soluble in the usual organic solvents:

0·1011 gave 0·2580 CO_2 and 0·0410 H_2O. C = 69·5; H = 4·5.

$C_{18}H_{14}O_5$ requires C = 69·7; H = 4·5 per cent.

Action of Alcoholic Ammonia on Ethyl Coumaranonecarboxylate.

The ester was not attacked when boiled with alcoholic ammonia for fifteen minutes, but the *ammonium* derivative was prepared by passing ammonia into an ethereal solution of the ester. It was analysed by boiling with sodium hydroxide and collecting the ammonia in standard acid:

0·1740 neutralised 7·5 c.c. $N/10$-H_2SO_4. NH_4 = 7·8.

$C_{11}H_9O_4(NH_4)$ requires NH_4 = 8·1 per cent.

The ammonium derivative slowly loses ammonia in the presence of water or on remaining for a long time in moist air.

Action of Grignard's Reagent on Ethyl Coumaranonecarboxylate.

The Grignard reagent, prepared by dissolving 2·4 grams of magnesium in 8 grams of methyl iodide mixed with dry ether, was slowly added to ethyl coumaranonecarboxylate (10·3 grams), dissolved in dry ether. A vigorous reaction took place, and a solid separated. The cooled mixture was treated with dilute sulphuric acid, the ethereal layer separated, and repeatedly extracted with sodium hydroxide. The alkaline extracts, when acidified, gave 10 grams of unchanged ester, showing that the ester had reacted entirely in the enolic form.

Action of Sodium on the Monoamide of Ethyl o-Carboxyphenoxyacetate.

The monoamide (8 grams) was dissolved in dry benzene, and the solution added to sodium (0·84 gram) suspended in dry benzene, when a vigorous reaction took place, with evolution of gas. The reaction was completed by boiling under reflux for three hours, only a trace of ammonia being evolved during the experiment.

The solid sodium compound which separated was dissolved in much water, the solution separated from benzene, and acidified with hydrochloric acid, when a white solid was precipitated. This was only moderately soluble in the usual organic solvents; when crystallised from alcohol it formed white needles melting at 221°. For analysis it was dried at 100°:

0·1110 gave 0·2262 CO_2 and 0·0454 H_2O. C=55·6; H=4·6.

0·1835 „ 11·3 c.c. N_2 (moist) at 17° and 763 mm. N=7·3.

$C_9H_9O_4N$ requires C=55·5; H=4·6; N=7·2 per cent.

The substance is evidently *o-carbamylphenoxyacetic acid*,

$NH_2·CO·C_6H_4·O·CH_2·CO_2H$.

Its alcoholic solution was titrated with *N*/10-sodium hydroxide, using phenolphthalein as indicator:

0·2100 required 10·8 c.c. *N*/10-NaOH. Equivalent weight=194·4.

$C_9H_9O_4N$ requires equivalent weight=195.

o-Carbamylphenoxyacetic acid crystallises from acetone in very light masses having the appearance of cotton-wool, and from glacial acetic acid in clusters of small needles. It is soluble in aqueous alkalis, and is precipitated unchanged on acidifying the solutions. On adding phenylhydrazine to an alcoholic solution of the acid, heat was evolved, and a salt separated in colourless needles, which melted at 177°. This salt was decomposed by cold sodium hydr-

oxide solution with the liberation of phenylhydrazine. On acidifying the alkaline solution, the original acid, melting at 221°, was deposited.

Hydrolysis of o-*Carbamylphenoxyacetic Acid.*

The acid was dissolved in 10 per cent. sodium hydroxide, and the solution heated on the water-bath until ammonia ceased to be evolved. On acidifying the product, white needles slowly separated. The substance melted at 192°, and its other properties corresponded with those of *o*-carboxyphenoxyacetic acid,

$$CO_2H\cdot C_6H_4\cdot O\cdot CH_2\cdot CO_2H$$

(Rössing, *Ber.*, 1884, **17**, 2995).

The same acid was formed by hydrolysing the monoamide of ethyl *o*-carboxyphenoxyacetate. The specimen prepared in this way also melted at 192°, and a mixture of the two melted at the same temperature

EAST LONDON COLLEGE,
UNIVERSITY OF LONDON.

CC.—*Coumaranone Derivatives. Part III. Acylazo-derivatives of Coumaranonecarboxylic Acid.*

By RICHARD WILLIAM MERRIMAN.

THE first known acylazo-derivative was benzoylazobenzene, $C_6H_5\cdot CO\cdot N:N\cdot C_6H_5$, which was prepared by Emil Fischer (*Annalen*, 1877, **190**, 67) by oxidising *s*-benzoylphenylhydrazine with yellow mercuric oxide. It was isolated as a dark red oil, which was decomposed by prolonged boiling with water. Benzoylazobenzene was re-examined by Hantzsch and Singer (*Ber.*, 1897, **30**, 319), who found that it combined with hydrogen chloride with the formation of benzoyl-*o*-chlorophenylhydrazine.

Fischer's compound remained an isolated example of the acylazo-class of compound until the year 1905, when the present author prepared benzeneazocarbonylcoumaranone,

$$C_6H_4{<}{\substack{O\\ CO}}{>}CH\cdot CO\cdot N:N\cdot C_6H_5,$$

and its phenylhydrazone (Part I., T., 1911, **99**, 914). These two substances and the corresponding tolyl derivatives have been subjected to more extended investigation.*

The orange azo-derivative still retains, in a greatly reduced

* Acylazo-derivatives have since been studied by Ponzio and Charrier (*Atti R. Accad. Sci. Torino*, 1909, **44**, 295), Gastaldi (*Gazzetta*, 1911, **41**, ii. 319) and Stollé (*Ber.*, 1912, **45**, 273).

degree, the acidic properties of the parent ester. Its acetyl derivative is hydrolysed by cold alkalis, and a solution of the sodium salt is alkaline to phenolphthalein, showing that the acidic properties of the coumaranone ester have been greatly reduced by the introduction of the azo-group. The acetyl derivative is also formed when phenylhydrazine is added to an alcoholic solution of ethyl acetocoumaranonecarboxylate and the mixture exposed to the oxidising action of the air. This method of preparation is of importance, as it proves that the coumaranone residue is still present in the azo-compound, which must therefore have the constitution assigned to it.

An alkaline solution of the azo-compound is reduced by zinc dust to benzenehydrazocarbonylcoumaranone,

$$C_6H_4{<}{}^{O}_{CO}{>}CH\cdot CO\cdot NH\cdot NHPh,$$

which is also produced directly by adding phenylhydrazine to an alcoholic solution of ethyl coumaranonecarboxylate in an atmosphere of hydrogen. The colourless alcoholic solution of the hydrazo-derivative is rapidly oxidised by the air, with formation of the orange azo-derivative.

It is remarkable that the ester group of ethyl coumaranonecarboxylate is attacked by phenylhydrazine, and not by alkalis or ammonia. The resistance of the ester to the latter reagents was attributed to salt-formation. This factor is absent in the case of the hydrazine, as there is no evidence of salt-formation when phenylhydrazine is added to an alcoholic solution of the coumaranone ester.

On reducing the azo-compound with stannous chloride or with sodium hyposulphite, the azo-group is broken in the normal manner, with the formation of aniline.

All the above reactions agree with the formula already proposed for the orange substance, which classes it as an acylazo-compound, but, unlike Fischer's benzoylazobenzene, it is not acted on by dry hydrogen chloride or by boiling acids or alkalis. This marked resistance to hydrolysis may be attributed to the acidic character of the substance.

The properties of the red phenylhydrazone also agree with the formula proposed for it. This substance forms an acetyl derivative which is hydrolysed by cold alkalis, the formula of which must be either

$$C_6H_4{<}{}^{O}_{C(:N\cdot NHPh)}{>}C:C(OAc)\cdot N:NPh \quad \text{or}$$

(I.)

$$C_6H_4{<}{}^{O}_{C(:N\cdot NAcPh)}{>}CH\cdot CO\cdot N:NPh$$

(II.)

Its colour is a much paler red than that of the phenylhydrazone itself; this points to a change of constitution, so that formula (I) is the more probable. An unstable, yellow sodium derivative is formed when an alcoholic solution of sodium ethoxide is added to a benzene solution of the azo-phenylhydrazone. The acidic properties of the red substance are, however, very weak, as it is insoluble in cold alkalis. When it is boiled with 50 per cent. potassium hydroxide a small amount dissolves, and on evaporating the mixture to dryness a yellow residue of the metallic derivative is left. On acidifying the residue practically the whole of the original red substance is recovered unchanged. This marked resistance of a phenylhydrazone to alkaline hydrolysis is not without analogy. For instance, Torrey and Brewster (*J. Amer. Chem. Soc.*, 1909, **31**, 1322) found that the phenylhydrazones of aceto-α-naphthol, and of pæonol, are insoluble in potassium hydroxide, and are not hydrolysed by boiling with this reagent.

Benzeneazocarbonylcoumaranonephenylhydrazone is quite stable towards boiling concentrated hydrochloric acid, but is readily hydrolysed by fuming hydrobromic acid with loss of phenylhydrazine and formation of benzeneazocarbonylcoumaranone. There is no doubt, therefore, that the red compound is the phenylhydrazone of the orange azo-compound.

The three tolylhydrazines react with ethyl coumaranonecarboxylate in the same way as phenylhydrazine, forming colourless hydrazo-compounds, orange azo-compounds, and red hydrazones of the latter substances, which have properties exactly similar to those of the corresponding compounds already discussed.

Absorption Spectra.

If the views expressed above are correct, the colourless hydrazo-compounds and the orange azo-compounds are derived from ethyl coumaranonecarboxylate by converting a carbethoxy-group into an acylhydrazo- and an acylazo-group respectively. The absorption curve of the coumaranone ester itself shows a deep band (Part II., preceding paper, Fig. 1), so that the effect produced by the above changes on the absorption curve might be somewhat obscured. In order to get a clearer idea of the effect of such substitutions, the absorption curves of benzoic acid, *s*-benzoylphenylhydrazine, and Fischer's benzoylazobenzene were compared. The benzoylazobenzene was prepared by Ponzio and Charrier's method (*loc. cit.*), and was obtained as a dark red solid, which forms orange solutions in alcohol. The three curves are drawn in Fig. 1. The curve for benzoic acid is reproduced from a paper by Hewitt, Pope, and Willett (T., 1912, **101**, 1772). This curve shows only general

absorption. In the case of *s*-benzoylphenylhydrazine the general absorption is much greater, and a very shallow band appears at $1/\lambda$ 3700. The general absorption for benzoylazobenzene reaches the visible spectrum, and the shallow band is now at $1/\lambda$ 3400.

It is clear that an acylhydrazo- or an acylazo-group does not

FIG. 2.

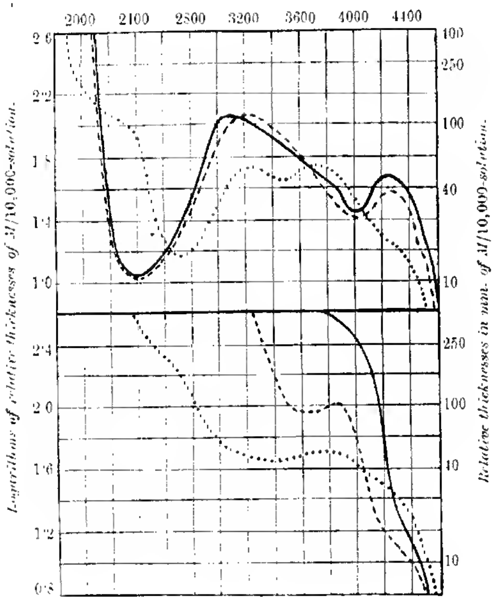


FIG. 1.

FIG. 1. ——— *Benzoic acid in alcoholic solution (reproduced).*
– – *s-Benzoylphenylhydrazine in alcoholic solution.*
.... *Benzoylazobenzene in alcoholic solution.*

FIG. 2. ——— *Benzeneazocarbonylcoumaranone in alcoholic solution.*
– – · *Acetyl derivative in alcoholic solution.*
.... *Benzeneazocarbonylcoumaranone in alcohol* + NaOH or NaOEt.

produce a well-marked band, so that any deep band present in the absorption curves of the compounds described in this communication must be due to the coumaranone residue present in the molecule.

The absorption curves of benzeneazocarbonylcoumaranone and of

its acetyl derivative are given in Fig. 2. The two curves are practically identical, which indicates that the azo-compound exists normally in the enolic form,

$$C_6H_4<\underset{C(OH)}{\overset{O}{}}>C\cdot CO\cdot N:NPh.$$

The addition of alkali to the parent ester fundamentally alters

FIG. 3.

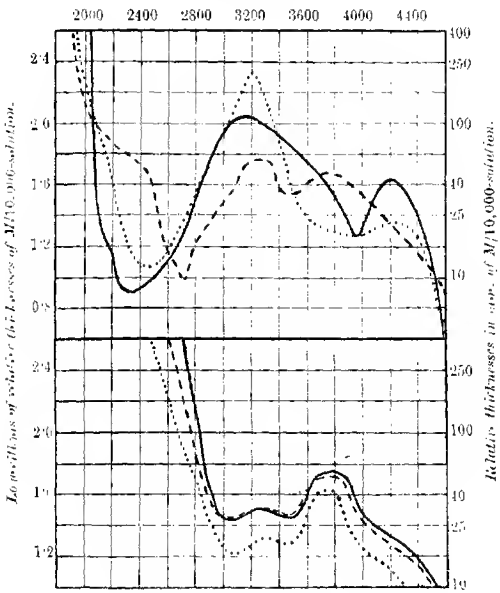


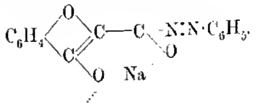
FIG. 4.

FIG. 3. ——— p-Tolueneazocarbonylcoumaranone in alcohol.
– – – – ,, ,, + NaOH or NaOEt.
.... Acetyl derivative of benzeneazocarbonylcoumaranonephenylhydrazone in alcohol.

FIG. 4. — — – – Benzenehydrazocarbonylcoumaranone in alcohol.
– – – ,, ,, – NaOH.
.... Ethyl hydroxycoumaranonecarboxylate in alcohol.

the character of its absorption curve (Part II., Fig. 1). In the case of the azo-derivative also, the addition of alkali to the solution greatly alters the character of the absorption curve. The same curve, drawn in Fig. 2, is produced by adding either aqueous sodium hydroxide solution or sodium ethoxide to the alcoholic

solution of the azo-compound. The azo-derivative itself exists in the enolic form. Therefore the change in constitution, indicated by the change in the absorption spectrum, produced on adding alkali, might be explained according to the modification of Hantzsch's theory proposed by Brannigan, Macbeth, and Stewart (this vol., p. 415) by means of the formula:



The absorption curve of *p*-tolueneazocarbonylcoumaranone, $C_6H_4<\genfrac{}{}{0pt}{}{-O-}{C(OH)}>C\cdot CO\cdot N{:}N\cdot C_6H_4Me$, is given in Fig. 3, together with the alteration produced on adding sodium hydroxide or sodium ethoxide. The curves are almost exactly similar to those of the corresponding benzeneazocarbonylcoumaranone, except that the bands are slightly more persistent, and are displaced to a small extent towards the red end of the spectrum.

The absorption spectrum of the colourless benzenehydrazocarbonylcoumaranone, $C_6H_4<\genfrac{}{}{0pt}{}{-O-}{CO}>CH\cdot CO\cdot NH\cdot NHPh$, is of a different type from that of the azo-derivative. The absorption curve, given in Fig. 4, shows two overlapping bands, and the addition of sodium hydroxide produces no marked change in the absorption spectrum, as was to be expected from the fact that the hydrazo-compound shows no acidic properties. It has, therefore, the ketonic constitution assigned to it above, which accounts for the great reduction in intensity, in its absorption curve, of the deep band present in the absorption curve of the enolic coumaranone ester.

The absorption curve of ethyl phenylhydrazinocoumaranonecarboxylate (Part II., *loc. cit.*), $C_6H_4<\genfrac{}{}{0pt}{}{-O-}{C(NH\cdot NHPh)}>C\cdot CO_2Et$, drawn in Fig. 4, is exactly similar to that of benzenehydrazocarbonyl coumaranone. The heads of the overlapping bands are at the same oscillation frequencies in the two cases, although they appear at greater dilutions in the spectrum of the hydrazino-compound. A comparison of the two formulæ assigned to these compounds explains the similarity of the selective absorption. They each contain the group $C_6H_5\cdot NH\cdot NH\cdot$, whilst neither contains an active enolic group. It is true that the coumaranone residue in the case of the hydrazino-compound has the same constitution as in the enolic compounds, $C_6H_4<\genfrac{}{}{0pt}{}{O}{C}>C-$, whilst in the hydrazo-derivative

it has the different constitution, $C_6H_4<^{O}_{C}>C-$. This probably accounts for the greater intensities of the vibrations in the case of the former compound.

The absorption spectrum of benzeneazocarbonylcoumaranonephenylhydrazone could not be examined owing to the small solubility of this compound in alcohol. The absorption curve of its acetyl derivative, which was sufficiently soluble to give a $M/2000$-solution, is given in Fig. 3. The curve is different from what one might expect, as it is very similar to that of the parent azo-compound, although no enolic group is present in the coumaranone part of the molecule.

A comparison of the formulæ given to the two compounds might explain the similarity of the absorption curves. These formulæ are:

$$C_6H_4<^{\quad O \quad}_{C(OH)}>C\cdot CO\cdot N:NPh \quad \text{and}$$

$$C_6H_4<^{\qquad O \qquad}_{C(:N\cdot NHPh)}>C:C(OAc)\cdot N:NPh.$$

The change in constitution of the coumaranone residue is from $C_6H_4<^{O}_{C}>C\cdot$ to $C_6H_4<^{O}_{C}>C:$, and this rearrangement has produced comparatively little change in the selective absorption.

Experimental.

Benzenehydrazocarbonylcoumaranone,

$$C_6H_4<^{O}_{CO}>CH\cdot CO\cdot NH\cdot NH\cdot C_6H_5.$$

Ethyl coumaranonecarboxylate (1 mol.) and phenylhydrazine (1 mol.) were dissolved in alcohol (free from air), and the solutions mixed in a flask from which air had been displaced by hydrogen. The mixture became red, and after the lapse of a day a considerable quantity of colourless leaflets was deposited, which was collected and washed with dilute acetic acid. The substance was readily soluble in the usual organic solvents, but during the recrystallisation from alcohol it became slightly yellow, owing to oxidation. It was recrystallised from carbon tetrachloride in large quantity in order to minimise the risk of oxidation, and formed colourless leaflets, which melted at 140—141°. This substance is insoluble in dilute ammonia, and therefore does not possess acidic properties; it is slowly hydrolysed by boiling sodium hydroxide solution with the liberation of phenylhydrazine:

0·1974 gave 0·4851 CO_2 and 0·0770 H_2O. C=67·0; H=4·3.
0·2473 „ 22·0 c.c. N_2 (moist) at 14° and 763 mm. N=10·6.
$C_{15}H_{12}O_3N_2$ requires C=67·2; H=4·5; N=10·4 per cent.

An alcoholic solution of this compound when exposed to the air yields benzeneazocarbonylcoumaranone, and when phenylhydrazine is simultaneously present the azophenylhydrazone (Part I., *loc. cit.*) is formed.

Derivatives of Benzeneazocarbonylcoumaranone,

$$C_6H_4<\overset{\text{——O——}}{C(OH)}>C\cdot CO\cdot N:N\cdot C_6H_5.$$

The *sodium* derivative is an orange powder obtained by adding sodium ethoxide to an ethereal solution of the azo-compound:

0·2518 gave 0·0610 Na_2SO_4. Na=7·85.
$C_{15}H_9O_3N_2$ requires Na=8·0 per cent.

The *acetyl* derivative, prepared by the aid of sodium acetate and acetic anhydride, crystallises from alcohol in brownish-yellow needles melting at 187°. It is more readily soluble in alcohol or benzene than the parent compound, and is easily hydrolysed by cold alkalis. This acetyl derivative is also formed when phenylhydrazine is added to an alcoholic solution of the acetyl derivative of ethyl coumaranonecarboxylate and the mixture left exposed to the air:

0·2065 gave 0·4996 CO_2 and 0·0765 H_2O. C=65·9; H=4·1.
0·2136 „ 16·5 c.c. N_2 (moist) at 14° and 759 mm. N=9·3.
$C_{17}H_{12}O_4N_2$ requires C=66·2; H=3·9; N=9·1 per cent.

The acetyl group was estimated by Herzig's method (*Monatsh.*, 1884, **5**, 90):

0·2357 gave 0·0882 $BaSO_4$, corresponding with 0·0453 acetic acid. One acetyl group would give 0·0459 acetic acid.

Reduction of Benzeneazocarbonylcoumaranone.

The azo-compound behaves towards reducing agents in the same way as azobenzene.

(*a*) Zinc dust was added to the hot alcoholic sodium hydroxide solution of the azo-compound until the orange-red solution became colourless. The hydrazo-derivative (*loc. cit.*) was recovered in a pure condition from this solution.

(*b*) On reducing the azo-compound with boiling hydrochloric acid and stannous chloride, or with sodium hyposulphite in sodium hydroxide solution, the azo-group was broken, with the formation of aniline. The other product of reduction was isolated as orange needles, which melted at 261° and sublimed without decomposition.

The substance contains nitrogen, and dissolves in concentrated sulphuric acid with the formation of a bright red solution:

0·0674 gave 0·1746 CO_2 and 0·0248 H_2O. C=70·7; H=4·1.

No simple formula can be deduced from these figures, and more of the substance is being accumulated for a complete investigation.

Derivatives of Benzeneazocarbonylcoumaranonephenylhydrazone.

The *sodium* derivative is an orange powder obtained by adding sodium ethoxide to the benzene solution of the azophenylhydrazone:

0·3157 gave 0·0620 Na_2SO_4. Na=6·35.

$C_{21}H_{15}O_2N_4Na$ requires Na=6·1 per cent.

The *acetyl* derivative forms orange-red needles melting at 139°, and is sparingly soluble in the usual organic solvents. It is readily hydrolysed by cold alkalis:

0·1938 gave 0·4927 CO_2 and 0·0802 H_2O. C=69·3; H=4·6.

0·2059 „ 23·90 N_2 (moist) at 14° and 759 mm. N=13·8.

$C_{23}H_{18}O_3N_4$ requires C=69·3; H=4·5; N=14·1 per cent.

The acetyl was estimated by Herzig's method (*loc. cit.*):

0·3523 gave 0·1017 $BaSO_4$, corresponding with 0·0523 acetic acid.

A monoacetyl derivative would give 0·0532 acetic acid.

Hydrolysis of Benzeneazocarbonylcoumaranonephenylhydrazone.

This phenylhydrazone is very resistant to hydrolytic agents. It was boiled for a day with concentrated hydrochloric acid without any hydrolytic action taking place. A large quantity was boiled with excess of 50 per cent. potassium hydroxide; the red substance gradually dissolved, and on evaporating the solution to dryness an orange-coloured residue of the potassium derivative of the red azophenylhydrazone was obtained. Hydrochloric acid was added to this residue, which was converted, apparently, entirely into the unchanged red compound; but a minute proportion of it was now soluble in dilute ammonia. The ammoniacal solution was acidified with dilute acid, and a small quantity of benzeneazocarbonylcoumaranone separated out. It was found during this work that fuming hydrobromic acid was a very powerful hydrolytic agent, and this acid readily decomposed the phenylhydrazone.

Fuming hydrobromic acid was added to the boiling alcoholic solution of the red phenylhydrazone, and the mixture boiled for twenty minutes. The alcohol was evaporated off, the residue made alkaline with sodium hydroxide, and steam blown through the mixture. Phenylhydrazine could be detected in the distillate, and the orange azo-compound was precipitated on acidifying the residue.

Similar colourless hydrazo-derivatives, orange azo-derivatives, and red azo-hydrazones were prepared by treating ethyl coumaranonecarboxylate with the three tolylhydrazines, in exactly the same way as already described in the case of phenylhydrazine.

p-*Toluenehydrazocarbonylcoumaranone* forms clusters of fine, colourless needles melting at 153°. It is hydrolysed by sodium hydroxide solution with the liberation of *p*-tolylhydrazine, and its alcoholic solution is oxidised by the air with the formation of the orange azo-compound:

0·1736 gave 0·4324 CO_2 and 0·0796 H_2O. C=68·0; H=5·1.
0·2253 „ 18·6 c.c. N_2 (moist) at 15° and 759 mm. N=9·7.
$C_{16}H_{14}O_3N_2$ requires C=68·1; H=5·0; N=9·9 per cent.

o-*Toluenehydrazocarbonylcoumaranone* forms long, colourless needles melting at 182°:

0·2573 gave 21·5 c.c. N_2 (moist) at 18° and 770 mm. N=9·9.
$C_{16}H_{14}O_3N_2$ requires N=9·9 per cent.

p-*Tolueneazocarbonylcoumaranone* crystallises in deep orange needles, melting at 187°:

0·1096 gave 0·2756 CO_2 and 0·0420 H_2O. C=68·6; H=4·3.
0·2315 „ 20·1 c.c. N_2 (moist) at 20° and 769 mm. N=10·2.
$C_{16}H_{12}O_3N_2$ requires C=68·6; H=4·3; N=10·0 per cent.

The *silver* derivative is a brick-red powder; the *sodium* derivative is an orange powder.

The *acetyl* derivative forms brown needles melting at 187°:

0·2418 gave 18·4 c.c. N_2 (moist) at 14° and 763 mm. N=8·8.
$C_{18}H_{14}O_4N_2$ requires N=8·7 per cent.

m-*Tolueneazocarbonylcoumaranone* melts at 162°, and forms a brick-red *silver* derivative, an orange *sodium* derivative, and a brown *acetyl* derivative:

0·1875 gave 0·4697 CO_2 and 0·0742 H_2O. C=68·4; H=4·4.
0·2316 „ 19·6 c.c. N_2 (moist) at 19° and 761 mm. N=9·8.
$C_{16}H_{12}O_3N_2$ requires C=68·6; H=4·3; N=10·0 per cent.

o-*Tolueneazocarbonylcoumaranone* forms deep orange needles melting at 193°:

0·1532 gave 0·3859 CO_2 and 0·0621 H_2O. C=68·6; H=4·5.
0·2436 „ 21 c.c. N_2 (moist) at 17° and 757 mm. N=10·2.
$C_{16}H_{12}O_3N_2$ requires C=68·6; H=4·3; N=10·0 per cent.

The *silver* derivative is a brick-red powder:

0·2736 gave 0·0779 Ag. Ag=28·5.
$C_{16}H_{11}O_3N_2Ag$ requires Ag=28·7 per cent.

The above azo-compounds, when reduced with zinc dust and sodium hydroxide, or hydrochloric acid and stannous chloride, or

sodium hyposulphite, behave in the same way as benzeneazocarbonylcoumaranone.

p-*Tolueneazocarbonylcoumaranone*-p-*tolylhydrazone* crystallises in ruby-red needles melting at 204°:

0·2145 gave 0·5671 CO_2 and 0·1041 H_2O. C=72·0; H=5·4.

0·2518 „ 31·2 c.c. N_2 (moist) at 14° and 763 mm. N=14·7.

$C_{23}H_{20}O_2N_4$ requires C=72·0; H=5·2; N=14·6 per cent.

o-*Tolueneazocarbonylcoumaranone*-o-*tolylhydrazone* forms deep red needles melting at 173°:

0·2037 gave 0·5345 CO_2 and 0·0970 H_2O. C=71·8; H=5·3.

0·1835 „ 22·4 c.c. N_2 (moist) at 16° and 762 mm. N=14·4.

$C_{23}H_{20}O_2N_4$ requires C=72·0; H=5·2; N=14·6 per cent.

The above azohydrazones are extremely resistant to hydrolytic agents, but are hydrolysed when boiled with fuming hydrobromic acid.

This series of communications formed part of a thesis approved for the D.Sc. degree of London University.

EAST LONDON COLLEGE.

CCI.—*Condensation of Acid Chlorides with the Ethyl Esters of* (a) *Cyanoacetic Acid,* (b) *Malonic Acid, and* (c) *Acetoacetic Acid. Part I.*

By CHARLES WEIZMANN, HENRY STEPHEN, and GANESH SAKHARAM AGASHE.

THE following account is an extension of a preliminary note (P., 1912, **28**, 103) on the condensation of acid chlorides with ethyl sodiomalonate, ethyl sodiocyanoacetate, and ethyl sodioacetoacetate, in which several such condensation products are described. It was thought probable that, by the preparation of this variety of substances, γ-substituted derivatives of ethyl acetoacetate might be obtained by submitting them to a suitable method of hydrolysis. With the exception of ethyl phthaliminoacetylmalonate and ethyl phthaliminopropionylmalonate, which gave ethyl phthaliminoacetoacetate and ethyl phthaliminopropionylacetate respectively when hydrolysed in the way to be described later, other condensation products led to the corresponding ketones on hydrolysis. This was the case, in particular, with the two examples described, namely,

ethyl ethoxyacetylmalonate and ethyl ethoxyacetylacetoacetate, both of which gave ethoxyacetone. Another method was therefore adopted in order to obtain ethyl γ-ethoxyacetoacetate, namely, by the condensation of ethyl acetate and ethyl ethoxyacetate, which proved to be a successful method for obtaining large quantities of this substance. In the case of ethyl phthaliminoacetoacetate, it is interesting to note that this substance has been isolated in the form of the enol- and keto-modifications. The examinations of these modifications will be pursued in the second part of this paper. Since the appearance of the preliminary note (*loc. cit.*) Pfaehler (*Ber.*, 1913, **46**, 1702) has published an account of several of the substances described by us, due to an oversight on the part of the author.*

Experimental.

Ethyl Ethoxyacetylcyanoacetate, $EtO{\cdot}CH_2{\cdot}CO{\cdot}CH(CN){\cdot}CO_2Et$.

Thirty-five grams (1 mol.) of ethoxyacetyl chloride, diluted with twice its own volume of dry ether, were added to two molecular proportions of ethyl sodiocyanoacetate (prepared by mixing 12·8 grams of finely divided sodium with 67 grams of ethyl cyanoacetate in dry ether), cooled in a freezing mixture. The mixture was allowed to remain in the cold for five hours, and then warmed gently on the steam-bath for the same period. The yellow sodium compound of the condensation product, which had separated during the reaction, was collected, washed with dry ether, and then decomposed with dilute sulphuric acid, the free condensation product being dissolved in ether. The dried ethereal extract was evaporated and the residue submitted to distillation under diminished pressure. A colourless liquid began to distil at 149°/16 mm., which gave a purple coloration with ferric chloride:

0·1331 gave 0·2670 CO_2 and 0·0826 H_2O. C=54·44; H=6·8.

$C_9H_{13}O_4N$ requires C=54·5; H=6·7 per cent.

The *copper* compound melts at 148°:

0·3402 gave 0·0572 CuO. Cu=13·63.

$(C_9H_{12}O_4N)_2Cu$ requires Cu=13·8 per cent.

Ethyl Phenoxyacetylcyanoacetate, $PhO{\cdot}CH_2{\cdot}CO{\cdot}CH(CN){\cdot}CO_2Et$.

This is prepared, in the same way as the previous compound, from phenoxyacetyl chloride and ethyl sodiocyanoacetate. It yields a *copper* compound, melting at 191°, and the free condensation product obtained from this copper compound crystallises from light petroleum, and melts at 14°:

* Private communication.

0·1721 gave 0·4015 CO_2 and 0·0852 H_2O. C=63·60; H=5·5.

$C_{13}H_{13}O_4N$ requires C=63·16; H=5·26 per cent.

Copper compound:

0·2713 gave 0·0397 CuO. Cu=11·6.

$(C_{13}H_{12}O_4N)_2Cu$ requires Cu=11·45 per cent.

Ethyl β-Chloropropionylcyanoacetate, $CH_2Cl·CH_2·CO·CH(CN)·CO_2Et$.

This is obtained by adding β-chloropropionyl chloride (1 mol.), diluted with an equal volume of ether, to ethyl sodiocyanoacetate (2 mols.), suspended in dry ether. The sodium compound of the condensation product is obtained and treated in the same way as before. The free condensation product is a white solid, crystallising from a mixture of benzene and light petroleum, and melts at 68°:

0·1852 gave 0·3220 CO_2 and 0·0867 H_2O. C=47·41; H=5·20.

0·1719 „ 0·1199 AgCl. Cl=17·2.

$C_8H_{10}O_3NCl$ requires C=47·17; H=4·91; Cl=17·4 per cent.

The *copper* compound crystallises from toluene in needles, melting at 159°:

0·3377 gave 0·0582 CuO. Cu=13·7.

$(C_8H_9O_3NCl)_2Cu$ requires Cu=13·50 per cent.

Ethyl γ-Ethoxyacetoacetate, $EtO·CH_2·CO·CH_2·CO_2Et$.

This compound has been prepared by condensing ethyl acetate with ethyl ethoxyacetate by means of sodium, according to the method described by Wahl and Doll (*Bull. Soc. chim.*, 1913, [iv], **13**, 468). The substance obtained is identical with that described by Sommelet (*Compt. rend.*, 1912, **154**, 706).

γ-Oximino-α-ethoxyacetone, $EtO·CH_2·CO·CH:NOH$.

Ethyl γ-ethoxyacetoacetate (5·2 grams) is dissolved in a solution of potassium hydroxide (1·8 grams) in water (69 c.c.), and a solution of sodium nitrite (2·2 grams) in water (9 c.c.) is added. After being kept for twenty-four hours at the ordinary temperature, the mixture is carefully acidified with *N*-sulphuric acid. The solution is then saturated with ammonium sulphate, and the oximino-compound extracted with ether. The residue, after evaporating the dried ethereal extract, solidifies to a paste of crystals, which, on crystallising from ethyl alcohol, are obtained in fine needles, melting and decomposing at 90°. The substance is soluble in cold water or ethyl alcohol, and sparingly so in benzene or light

petroleum, from which also it can be crystallised. It dissolves in alkaline solutions with a yellow colour:

0·1050 gave 0·1749 CO_2 and 0·0629 H_2O. C=45·44; H=6·66.
0·1320 „ 12·6 c.c. N_2 (moist) at 21° and 757 mm. N=10·84.
$C_5H_9O_3N$ requires C=45·8; H=6·87; N=10·7 per cent.

Ethyl Ethoxyacetylmalonate, $EtO·CH_2·CO·CH(CO_2Et)_2$.

This compound was obtained by adding ethoxyacetyl chloride (1 mol.), diluted with its own volume of dry benzene, to two molecular proportions of ethyl sodiomalonate, suspended in dry benzene, the mixture being cooled in ice during the addition of the chloride. After twelve hours, the mixture was warmed on the steam-bath for three hours, when the sodium compound of the condensation product separated as a yellow solid. This was collected and decomposed with dilute sulphuric acid, the free condensation product being dissolved in ether. The dried ethereal extract was evaporated, and the residue submitted to distillation under diminished pressure. The condensation product is a colourless oil, which boils at 165°/19 mm., and gives a purple coloration with ferric chloride. The copper compound crystallises from toluene or ethyl acetate in blue needles, melting at 104°, from which the free product can be obtained:

0·1711 gave 0·3338 CO_2 and 0·1135 H_2O. C=53·2; H=7·36.
$C_{11}H_{18}O_6$ requires C=53·66; H=7·32 per cent.

Copper compound:

0·2101 gave 0·0291 CuO. Cu=11·2.
$(C_{11}H_{17}O_6)_2Cu$ requires Cu=11·4 per cent.

Ethyl ethoxyacetylacetoacetate, $EtO·CH_2·CO·CHAc·CO_2Et$, is prepared in a similar way to the previous compound by adding ethoxyacetyl chloride (1 mol.) to ethyl sodioacetoacetate (2 mols.) suspended in dry benzene. It is purified by means of its copper compound, and is a colourless liquid boiling at 132—133°/12 mm., and giving a purple coloration with ferric chloride:

0·0894 gave 0·1816 CO_2 and 0·0635 H_2O. C=55·4; H=7·8.
$C_{10}H_{16}O_5$ requires C=55·4; H=7·4 per cent.

The *copper* compound, after crystallisation from benzene, decomposes at 110°.

Behaviour of Ethyl Ethoxyacetylmalonate and Ethyl Ethoxyacetylacetoacetate on Hydrolysis in Neutral Solution.

Ten c.c. of ethyl ethoxyacetylmalonate were mixed with 5 c.c. of water, and heated in a sealed tube for one hour at 250°. The

contents of the tube were neutralised with *N*-sodium carbonate solution, and the solution was distilled in a current of steam. The distillate was saturated with potassium carbonate, and extracted several times with ether. The dry ethereal extract gave an oil, which was treated with a dilute acetic acid solution of *p*-nitrophenylhydrazine, and the *p*-nitrophenylhydrazone of ethoxyacetone was obtained, which crystallised from benzene and light petroleum in bright orange leaves, melting at 102° (*Ann. Chim. Phys.*, 1906, [viii], **9**, 516).

The same result was obtained on similar treatment of ethyl ethoxyacetylacetoacetate with water in a sealed tube at 250° for one hour.

It was observed that in both cases very little acid hydrolysis had taken place, from the fact that a very small quantity of *N*-sodium carbonate solution was required for neutralisation.

Ethyl Phenoxyacetylacetoacetate, $PhO\cdot CH_2\cdot CO\cdot CHAc\cdot CO_2Et$.

Phenoxyacetyl chloride and ethyl sodioacetoacetate were condensed according to the previous method; the product is best purified by means of the copper compound, from which it is obtained as an oil distilling at 174°/14 mm., and solidifying to a white, crystalline solid, melting at 84—86°; it gives the ferric chloride reaction:

0·1254 gave 0·2895 CO_2 and 0·0681 H_2O. C = 63·6; H = 6·06.
$C_{11}H_{16}O_5$ requires C = 63·63; H = 6·06 per cent.

Ethyl Amyloxyacetylacetoacetate, $C_5H_{11}\cdot O\cdot CH_2\cdot CO\cdot CHAc\cdot CO_2Et$.

Molecular quantities of ethyl sodioacetoacetate and amyloxyacetyl chloride are condensed in dry ether. The product is a colourless liquid, boiling at 176°/14 mm., which gives a *copper* compound, and a violet coloration with ferric chloride:

0·1148 gave 0·3195 CO_2 and 0·1069 H_2O. C = 60·1; H = 8·5.
$C_{13}H_{22}O_5$ requires C = 60·48; H = 8·2 per cent.

Ethyl β-Amyloxypropionylacetoacetate,
$C_5H_{11}\cdot O\cdot CH_2\cdot CH_2\cdot CO\cdot CHAc\cdot CO_2Et$.

β-Amyloxypropionyl chloride (1 mol.) is condensed with ethyl sodioacetoacetate (2 mols.) in suspension in dry ether; the mixture is kept for forty-eight hours at the ordinary temperature, and then warmed for four hours on the steam-bath. It is then acidified with dilute sulphuric acid, and the condensation product dissolved in ether. After evaporating the dried ethereal extract, the residual

oil distilled at 175°/12 mm. It was purified by means of the *copper* compound, and is a colourless liquid:

0·1386 gave 0·3094 CO_2 and 0·1097 H_2O. C=60·88; H=8·8.
$C_{14}H_{24}O_5$ requires C=61·76; H=8·8 per cent.

Ethyl β-Amyloxypropionylmalonate,
$C_5H_{11}\cdot O\cdot CH_2\cdot CH_2\cdot CO\cdot CH(CO_2Et)_2$.

This is prepared according to the above method by condensing β-amyloxypropionyl chloride (1 mol.) with ethyl sodiomalonate (2 mols.). The substance is a colourless liquid, boiling at 190°/18 mm.:

0·1164 gave 0·2539 CO_2 and 0·0895 H_2O. C=59·51; H=8·55.
$C_{15}H_{26}O_6$ requires C=59·45; H=8·61 per cent.

Ethyl Phthaliminoacetoacetate (Keto-form),
$C_6H_4<{CO \atop CO}>N\cdot CH_2\cdot CO\cdot CH_2\cdot CO_2Et$.

This substance was prepared by condensing phthaliminoacetyl chloride (1 mol.) with ethyl sodiomalonate (1 mol.) suspended in dry benzene. After twelve hours the mixture is warmed on the steam-bath for three hours, and poured into dilute sulphuric acid until completely acidified; the benzene layer is then extracted with sodium carbonate solution several times, and the benzene afterwards removed by distillation under diminished pressure. The oily residue solidified on cooling, and on crystallisation from ethyl alcohol was obtained in small, white needles, melting at 119°. This substance does not give a coloration with ferric chloride:

0·1506 gave 0·3367 CO_2 and 0·0570 H_2O. C=61·00; H=4·3.
0·2328 „ 10·7 c.c. N_2 (moist) at 20° and 756 mm. N=5·34.
$C_{14}H_{13}O_5N$ requires C=61·09; H=4·7; N=5·10 per cent.

Ethyl Phthaliminoacetoacetate (Enol-form).

If the alcoholic solution of the above substance is mixed with a cold alcoholic solution of an equimolecular quantity of potassium ethoxide, a yellow, crystalline potassium compound is obtained. This is dissolved in water and decomposed with cold dilute acetic acid, or by means of a current of carbon dioxide; the compound set free is dissolved in ether, and the dry ethereal extract, on evaporation, leaves a pale yellow, crystalline solid, which crystallises from ethyl alcohol in small, yellow needles, melting at 70°. This substance gives a deep purple coloration with ferric chloride, and is thus the enolic modification of ethyl phthaliminoacetoacetate:

0·1184 gave 0·2648 CO_2 and 0·0526 H_2O. C = 61·00; H = 4·93.
0·1522 „ 6·4 c.c. N_2 (moist) at 15° and 765 mm. N = 5·18.
$C_{14}H_{13}O_5N$ requires C = 61·09; H = 4·7; N = 5·10 per cent.

Ethyl Phthaliminoacetylchloromalonate,

$$C_6H_4<\!\!\genfrac{}{}{0pt}{}{CO}{CO}\!\!>N\cdot CH_2\cdot CO\cdot CCl(CO_2Et)_2.$$

Phthalylglycyl chloride (1 mol.) is treated with the potassium compound of ethyl chloromalonate (1 mol.) suspended in dry benzene. The condensation product crystallises from methyl alcohol in needles, melting at 99° (Pfaehler gives 95—96°). (Found, Cl = 8·93. $C_{17}H_{16}O_7NCl$ requires Cl = 9·29 per cent.)

On distillation in a current of steam in presence of dilute sulphuric acid, it yields phthaliminoacetic acid.

UNIVERSITY, MANCHESTER.

CCII.—*The Action of Sulphur Chloride and of Thionyl Chloride on Metallic Salts of Organic Acids: Preparation of Anhydrides.*

By WILLIAM SMITH DENHAM and HILDA WOODHOUSE (Carnegie Scholar).

THE preparation of anhydrides of organic acids by the action of sulphur chloride on metallic salts in the presence of an indifferent solvent has already been described by one of the authors (T., 1909, **95**, 1237). The reaction proceeds in two stages, which are represented for the case of silver benzoate by the equations:

$$(1) \qquad 2C_6H_5\cdot CO_2Ag + Cl_2S_2 = (C_6H_5\cdot CO_2)_2S_2 + 2AgCl.$$
$$(2) \qquad 2(C_6H_5\cdot CO_2)_2S_2 = 2(C_6H_5\cdot CO)_2O + SO_2 + 3S.$$

The intermediate compounds of the general formula $(R\cdot CO_2)_2S_2$ can, as a rule, be isolated, but very soon decompose spontaneously in the manner indicated by equation (2).

A compound of the type $(R\cdot CO_2)_2S_2$ may be regarded as a mixed anhydride of the organic acid and of an unknown sulphur acid, $S_2(OH)_2$, of which sulphur monochloride, S_2Cl_2, would be the chloride. Other derivatives of this acid are already known, as, for example, the substituted amides $S_2(NMe_2)_2$ and $S_2(NEt_2)_2$, which are readily obtained by the interaction of the alkylamines and

sulphur chloride (Michaelis, *Ber.*, 1895, **28**, 165). Lengfeld (*Ber.*, 1895, **28**, 449) describes esters which he terms methyl and ethyl thiosulphites, obtained by the action of sulphur chloride on sodium methoxide and on sodium ethoxide in the presence of light petroleum. The authors, although their attempts to prepare these compounds were unsuccessful and yielded only chlorinated products which evolved hydrochloric acid on keeping, propose to retain the term "thiosulphite" as a convenient designation for the acyl compounds now described.

The acyl thiosulphites should be compounds of considerable interest, and in the hope of isolating stable representatives of this class the salts of a large number of acids have been subjected to the reaction with sulphur chloride, but, despite minor variations in the degree of stability, a stable acyl thiosulphite was not obtained. The reaction, which proceeds smoothly as a rule, is, however, of general application as a method of preparing anhydrides, but fails in the cases of hydroxy- and amino-acids when more complex reactions occur, and it is inferior as a practical method to that in which thionyl chloride is used (P., 1909, **25**, 294). In this method equivalent quantities of the silver salt and thionyl chloride are shaken together in presence of ether or other indifferent solvent, when silver chloride, sulphur dioxide, and the anhydride are formed, the last-mentioned product being obtained nearly pure on filtration and removal of the solvent. The formation of benzoic anhydride in this manner is indicated by the equation:

$$2C_6H_5{\cdot}CO_2Ag + SOCl_2 = (C_6H_5{\cdot}CO)_2O + SO_2 + 2AgCl.$$

This method also is a general one, but, as with sulphur dioxide, fails in the case of amino-acids, whilst the reaction with hydroxy-acids appears to be abnormal. The preparation of bromoacetic anhydride from the sodium salt according to this method is described in the experimental part of this paper.

The salts of hydroxy-acids are exceptional in their behaviour towards both sulphur chloride and thionyl chloride. Sulphur chloride has little action on silver glycollate, it reacts only slowly with silver malate, whilst, with silver mandelate, reaction occurs more readily, but apparently in a less simple manner than usual. Thionyl chloride, on the other hand, reacts at once with all three salts. In the case of silver glycollate, a white, crystalline compound separates from the filtrate, the composition of which is represented by the formula $(HO{\cdot}CH_2{\cdot}CO_2)_2SO$; similar compounds are formed from silver mandelate and silver malate, although they have not been isolated in a pure condition. All these compounds part with sulphur dioxide only slowly in dry air even when they

are heated. The formation of intermediate thionyl compounds was not observed in the preparation of anhydrides of other acids by this method, and as silver methoxyacetate does not yield a thionyl compound, it appears probable that the hydroxyl group plays a specific part in the reaction when salts of hydroxy-acids are used. Jarrard, however, on applying the method to the preparation of mellitic trianhydride, noted the formation of an intermediate compound which was not decomposed at once by boiling the solution (P., 1913, **29**, 106). From the products of the reactions between thionyl chloride and the salts of these hydroxy-acids it has been found possible to separate substances of undetermined constitution which have the same percentage composition as would be possessed by anhydrides of normal type; the conditions for their preparation having now been established, their investigation will be continued. The anhydride derived from malic acid is crystalline, and appears to be a chemical individual; it differs, probably, from the substance of the same composition obtained by Walden by heating the acid. The anhydride derived from mandelic acid is a glass, and, whilst similar to the anhydrides described by Bischoff and Walden (*Annalen*, 1899, **279**, 129), Staudinger (*Ber.*, 1911, **44**, 545), and Stutz (*Ber.*, 1911, **44**, 3485), may be represented by a simpler empirical formula.

The results just recapitulated are of some interest in connexion with the much-discussed question of the constitution of sulphur chloride. At present opinion seems to be divided between the constitutions represented by the formulæ $\begin{array}{l}S\cdot Cl\\ \mid\\ S\cdot Cl\end{array}$ and $S{:}S{<}^{Cl}_{Cl}$, the latter representing the compound as the sulphur analogue of thionyl chloride. Although either formula is sufficient for the representation of the reactions at present under consideration, it may be pointed out, in view of the possible similarity in constitution of the two chlorides, that the analogy between the two series of reactions may be made more striking on the assumption that the first product of the interaction of the silver salt and thionyl chloride is the unstable mixed anhydride $(R\cdot CO_2)_2SO$, an assumption which finds support in Jarrard's observation just mentioned, even if the formation of a thionyl compound from silver glycollate is thought to be inadmissible as evidence on account of the possible participation of the hydroxyl groups in the reaction. Further, the intermediate compound, $(R\cdot CO_2)_2S_2$, derived from sulphur chloride may be regarded as giving as the first products of decomposition the anhydride $(R\cdot CO)_2O$, and an oxide of sulphur, S_2O, which immediately decomposes into sulphur dioxide and sulphur.

The fact that the decomposition of the acyl thiosulphite proceeds as a reaction of the first order is in harmony with this view. The changes which occur would then be represented as follows:

$$2R\cdot CO_2Ag + SOCl_2 = (R\cdot CO_2)_2SO + 2AgCl \qquad 2R\cdot CO_2Ag + S_2Cl_2 = (R\cdot CO_2)_2S_2 + 2AgCl$$
$$(R\cdot CO_2)_2SO = (R\cdot CO)_2O + SO_2 \qquad (R\cdot CO_2)_2S_2 = (R\cdot CO)_2O + S_2O$$
$$2S_2O = SO_2 + 3S$$

It may not be superfluous to point out that the analogy extends further, for, if silver benzoate is treated in the presence of ether with twice the quantity of thionyl chloride that is required for the formation of the anhydride, the filtrate, on evaporation of the solvent, gives benzoyl chloride in good yield. The preparation of acid chlorides of hydroxy-acids according to this method has been patented (Kopetschni and Karczag, Fr. Pat. 450227). Similarly, although less readily and less smoothly, sodium benzoate when heated with sulphur chloride in equimolecular proportions gives essentially benzoyl chloride, sodium chloride, sulphur dioxide, and free sulphur (Carius, *Annalen*, 1858, **106**, 291). Benzoyl chloride is formed also when benzoic anhydride is heated with sulphur chloride. The following equations represent similar reactions:

$$(C_6H_5\cdot CO)_2O + SOCl_2 = 2C_6H_5\cdot COCl + SO_2.$$
$$2(C_6H_5\cdot CO)_2O + 2S_2Cl_2 [= 4C_6H_5\cdot COCl + 2S_2O] = 4C_6H_5\cdot COCl + SO_2 + 3S.$$

The two stages represented by the equations:

$$2C_6H_5\cdot CO_2Na + 2S_2Cl_2 = (C_6H_5\cdot CO)_2S + 2SOCl_2 + Na_2S = 2C_6H_5\cdot COCl + 2NaCl + SO_2 + 3S,$$

in which Carius thought the reaction between sodium benzoate and sulphur chloride to occur, appear to be less probable.

EXPERIMENTAL.

The products obtained by the action of sulphur chloride on sodium benzoate and on the silver salts of acetic, propionic, benzoic, *o*-toluic, *m*-toluic, *p*-toluic, and phenylacetic acids have already been described (T., 1909, **95**, 1235). Additional data are here given regarding the benzoyl compound, and a record of experiments with salts of other acids, which were carried out in the search for a stable compound of the type.

Action of Sulphur Chloride on Silver Salts.

Sulphur Chloride and Silver Benzoate.—12·5 Grams (instead of 11·5 grams) of silver benzoate suspended in 50 c.c. of dry ether

were treated with 3·4 grams of sulphur chloride, and the mixture was shaken vigorously. After filtration from the silver chloride and removal of the ether, 7·5 grams of benzoyl thiosulphite were obtained as a colourless syrup, which soon crystallised with marked evolution of heat, and afterwards decomposed. From the products of decomposition 5·6 grams of the crude anhydride were extracted by means of ether, and 0·96 gram of sulphur was left. The calculated quantities (reckoning on the amount of sulphur chloride used) are 7·6 grams of benzoyl thiosulphite, 5·65 grams of benzoic anhydride, and 0·95 gram of sulphur, if the reactions which occur are represented by the equations:

$$2C_6H_5\cdot CO_2Ag + S_2Cl_2 = (C_6H_5\cdot CO_2)_2S_2 + 2AgCl.$$
$$2(C_6H_5\cdot CO_2)_2S_2 = 2(C_6H_5\cdot CO)_2O + SO_2 + 3S.$$

The crude anhydride was now mixed with 3·4 grams of sulphur chloride and heated under reflux for four hours. On extraction of the product with ether, 1 gram of sulphur was left, and the ethereal extract contained 6 grams of dissolved matter, which consisted chiefly of benzoyl chloride. The calculated amounts are 1·2 grams of sulphur and 7·1 grams of benzoyl chloride on the assumption that the reaction is represented by the equation:

$$2(C_6H_5\cdot CO)_2O + 2S_2Cl_2 = 4C_6H_5\cdot COCl + SO_2 + 3S.$$

Determination of the Velocity Constant for the Decomposition of Benzoyl Thiosulphite.

The sulphur dioxide evolved from a solution of the compound in boiling toluene was expelled from the containing flask by means of a regular current of dry carbon dioxide, and passed through a reflux condenser into a dilute solution of iodine in potassium iodide, which was replaced from time to time.

The total volume of iodine solution used (after some hours) $= a =$ 71·2 c.c.

Minutes.	x = c.c. Iodine.	$a - x$.	$1/t \log a/a - x$.
10	9·1	62·1	0·0059
26	21·4	49·8	0·0060
45	33·0	38·2	0·0060
71	43·7	27·5	0·0059
85	48·2	23·0	0·0058

Sulphur chloride and silver n-*butyrate* gave a viscous liquid, which closely resembled the acetyl compound:

0·3199 gave 0·6220 $BaSO_4$. S = 26·71.

0·4805, in 12·25 benzene, gave $\Delta t = -0·08°$. M.W. = 213.

$C_8H_{14}O_4S_2$ requires S = 26·89 per cent. M.W. = 238.

Sulphur chloride and silver isobutyrate reacted in the usual way, but the intermediate product was so unstable that a sample could not be obtained for analysis.

Sulphur chloride and silver isovalerate gave an oil which decomposed almost immediately after preparation:

0·3437 gave 0·5954 $BaSO_4$. S=23·76.

0·3972, in 9·07 benzene, gave $\Delta t = -0·055°$. M.W.=233.

$C_{10}H_{18}O_4S_2$ requires S=24·06 per cent. M.W.=266.

The decomposition products from these preparations reacted immediately with aniline, giving about the same yields of anilide as is obtained from acetic anhydride.

Sulphur chloride and silver palmitate gave an intermediate product, which was only sparingly soluble in ether. The reaction mixture was therefore warmed, and, on filtering the solution, palmityl thiosulphite crystallised in soft, feathery crystals, which closely resembled those of palmitic acid:

0·2417 gave 0·2050 $BaSO_4$. S=11·64.

0·7049, in 25·05 benzene, gave $\Delta t = -0·30°$. M.W.=469.

$C_{32}H_{62}O_4S_2$ requires S=11·15 per cent. M.W.=574.

The compound decomposed normally, but the anhydride was not easily obtained free from sulphur.

Sulphur chloride and silver α-naphthoate gave a product which separated from the ethereal solution as a white, crystalline mass:

0·3212 gave 0·3688 $BaSO_4$. S=15·77.

$C_{22}H_{14}O_4S_2$ requires S=15·76 per cent.

The anhydride presumably formed when this substance decomposed, either at the ordinary temperature or on heating, could not be obtained free from a small quantity of sulphur. After dissolving it in a solution of sodium hydroxide and filtering from the undissolved sulphur, addition of hydrochloric acid to the solution precipitated α-naphthoic acid in a pure state.

Sulphur chloride and silver monochloroacetate reacted normally, and yielded a compound which is similar to the acetyl compound, but is less stable:

0·4750 gave 0·8997 $BaSO_4$. S=26·02.

0·649, in 10·51 benzene, gave $\Delta t = -1·57°$. M.W.=197.

$C_4H_4O_4Cl_2S_2$ requires S=25·50 per cent. M.W.=251.

Sulphur chloride and silver tribromoacetate gave a dark brown oil, which deposited sulphur before the ether was completely removed.

Sulphur chloride and the silver bromobenzoates reacted normally. The products are probably less stable than the benzoyl compound;

for this reason and on account of its sparing solubility the para-compound was not obtained pure:

o-compound: 0·2162 gave 0·2070 $BaSO_4$. S = 13·15.
m-compound: 0·4156 „ 0·4272 $BaSO_4$. S = 14·11.
p-compound: 0·2350 „ 0·1730 $BaSO_4$. S = 10·11.
$C_{14}H_8O_4Br_2S_2$ requires S = 13·79 per cent.

Sulphur chloride and the silver nitrobenzoates react normally, and the products which, like the anhydrides themselves, are only sparingly soluble in the usual solvents, undergo normal decomposition. The reactions were carried out in the presence of carbon disulphide, and the anhydrides were extracted from the decomposition products by means of ethyl acetate, and were recrystallised from that solvent:

o-compound: 0·3352 gave 0·4194 $BaSO_4$. S = 17·19.
m-compound: 0·1894 „ 0·2150 $BaSO_4$. S = 15·56.
p-compound: 0·1062 „ 0·1204 $BaSO_4$. S = 15·55.
$C_{14}H_8O_8N_2S_2$ requires S = 16·16 per cent.

Sulphur chloride and the silver aminobenzoates react at once in presence of ether. After concentration of the yellow ethereal solution and addition of light petroleum a yellowish-brown substance is precipitated, the sulphur content of which agrees approximately with that of a substance of the formula $(NH_2{\cdot}C_6H_4{\cdot}CO_2)_2S_2$, but this compound, if formed, is not of the usual type, and although some sulphur separates on keeping, the residue still contains combined sulphur.

Sulphur Chloride and Silver Salts of Hydroxy-acids.—Reaction between sulphur chloride and silver glycollate or silver malate proceeds only slowly in the presence of ether. The products are syrups which deposit sulphur and evolve sulphur dioxide, but no definite compounds were obtained from the decomposition products. In the case of silver mandelate reaction occurs at once on the addition of an ethereal solution of sulphur chloride to a suspension of the salt in ether. After filtration from the silver chloride and removal of part of the ether by distillation, addition of light petroleum causes the precipitation of a crystalline paste, which at once decomposes with deposition of sulphur and evolution of sulphur dioxide. The only pure substance that could be obtained from the decomposition product was mandelic acid.

The behaviour of sulphur chloride towards the silver salts of the hydroxybenzoic acids appears to be irregular.

Action of Thionyl Chloride on Silver Salts.

Action of Thionyl Chloride on Silver Benzoate.—4·7 Grams of silver benzoate (instead of 4·6 grams) were treated with 1·2 grams of thionyl chloride in the presence of 30 c.c. of ether. On distillation of the ether from the filtered solution, 2·1 grams of nearly pure benzoic anhydride were obtained. The calculated amount is 2·3 grams. The method has been further tested by the preparation in a similar manner of the anhydrides of acetic, monobromoacetic, palmitic, *o*-bromobenzoic, *m*-nitrobenzoic, and α-naphthoic acids. The preparation of the anhydride of *o*-bromobenzoic acid does not appear to have been previously recorded.

Preparation of o-*Bromobenzoic Anhydride.*—0·6 Gram of thionyl chloride was shaken with 3·2 grams (instead of 3·1 grams) of silver bromobenzoate in the presence of 60 c.c. of ether. 1·65 Grams of a yellow, crystalline substance separated from the viscous liquid which remained after removal of the ether by distillation from the filtered solution. The calculated yield of anhydride is 1·99 grams. The yellow impurity was removed by recrystallisation from ether after treatment with animal charcoal. The anhydride melts at 75—76°:

0·1512 gave 0·1470 AgBr. Br=41·37.

$C_{14}H_8O_3Br_2$ requires Br=41·65 per cent.

Gerhardt (*Annalen*, 1853, **87**, 158) was unable to obtain *m*-nitrobenzoic anhydride in the pure state by the action of phosphoryl chloride on the sodium salt. Autenrieth (*Ber.*, 1901, **34**, 181) gives 47° as the melting point for the anhydride prepared by boiling *m*-nitrobenzoic acid with acetic anhydride. The melting point of the anhydride prepared as described below was 160°.

Preparation of m-*Nitrobenzoic Anhydride.*—Six grams of silver *m*-nitrobenzoate (instead of 5·5 grams) were shaken with 1·2 grams of thionyl chloride in 30 c.c. of ether. The ether was removed by distillation, and the residual mixture of silver chloride and anhydride was extracted twice by boiling with 20 c.c. of ethyl acetate each time. The crude product was recrystallised from ethyl acetate:

0·2116 gave 0·4114 CO_2 and 0·0502 H_2O. C=53·02; H=2·63.

$C_{14}H_8O_7N_2$ requires C=53·16; H=2·53 per cent.

Preparation of Bromoacetic Anhydride.—Twenty grams of thionyl chloride were added gradually to a slightly warm mixture of 55 grams of sodium bromoacetate (Bischoff and Walden, *Annalen*, 1894, **46**, 279) and 250 c.c. of dry light petroleum contained in a 500 c.c. flask fitted with a reflux condenser and a

mercury-sealed stirrer. After the vigorous reaction was over the mixture was boiled to remove the remaining sulphur dioxide, and then filtered while still warm; the residual sodium chloride was washed with ether, and further extracted for some hours with the same solvent in a Soxhlet apparatus. The combined solutions were washed with a cold aqueous solution of sodium hydrogen carbonate and dried with anhydrous magnesium sulphate. The total yield after purification by fractional distillation under diminished pressure was 80 per cent. of the calculated amount.

Thionyl Chloride and Silver Glycollate.—To 1·9 grams of silver glycollate (1 mol.) suspended in 30 c.c. of ether, 0·6 gram of thionyl chloride ($\frac{1}{2}$ mol.) was added, and the mixture shaken. The syrup left after filtration and distillation of the ether crystallised suddenly. The compound was purified by dissolving it in ether and reprecipitating with light petroleum, the process being repeated two or three times until the substance was free from halogen:

0·1984 gave 0·1796 CO_2 and 0·0536 H_2O. C=24·69; H=3·00.
0·2350 „ 0·2752 $BaSO_4$. S=15·99.
$C_4H_6O_7S$ requires C=24·24; H=3·03; S=16·16 per cent.

The compound has thus the composition of a thionyl derivative of glycollic acid. The decomposition of this substance, although apparent very soon after its preparation by the odour of sulphur dioxide, does not proceed rapidly; a sample which had been left in an evacuated desiccator at the ordinary temperature still contained, nine days after preparation, 11·32 per cent. of sulphur. A small quantity of the thionyl compound which had remained for about a fortnight at the ordinary temperature was washed quickly with ether, which removed a more soluble portion, and analysed:

0·1190 gave 0·1574 CO_2 and 0·0482 H_2O. C=36·07; H=4·50.
$C_4H_6O_5$ requires C=35·82; H=4·48 per cent.

The substance has thus the composition of an anhydride of glycollic acid. It softens at about 90°, and is completely melted at 102—103°.

Thionyl chloride and silver methoxyacetate react at once without the formation of a thionyl compound. The reaction appears to proceed normally; fractional distillation of the product under diminished pressure did not, however, yield the anhydride in the pure state.

Thionyl chloride and silver mandelate in the presence of ether yield a crystalline thionyl derivative, mixed, however, with chlorinated products. If, after repeated solution in ether and reprecipitation with light petroleum, it is heated for several days at 60—70°

in a current of dry carbon dioxide to remove sulphur dioxide and then extracted with cold benzene, a glass-like product is obtained on removal of the benzene in a vacuum, which, although of undetermined constitution and possibly a mixture, has a composition nearly that of an anhydride of normal type:

0·1650 gave 0·4020 CO_2 and 0·0760 H_2O. C=66·45; H=4·71.
$C_{16}H_{14}O_5$ requires C=67·13; H=4·90 per cent.

0·5365 gram neutralised 75·3 c.c. $N/20$-baryta solution, in which it dissolved on boiling; 70·6 c.c. would be required by the same quantity of mandelic acid, and 75·0 c.c. by an anhydride, $C_{16}H_{14}O_5$.

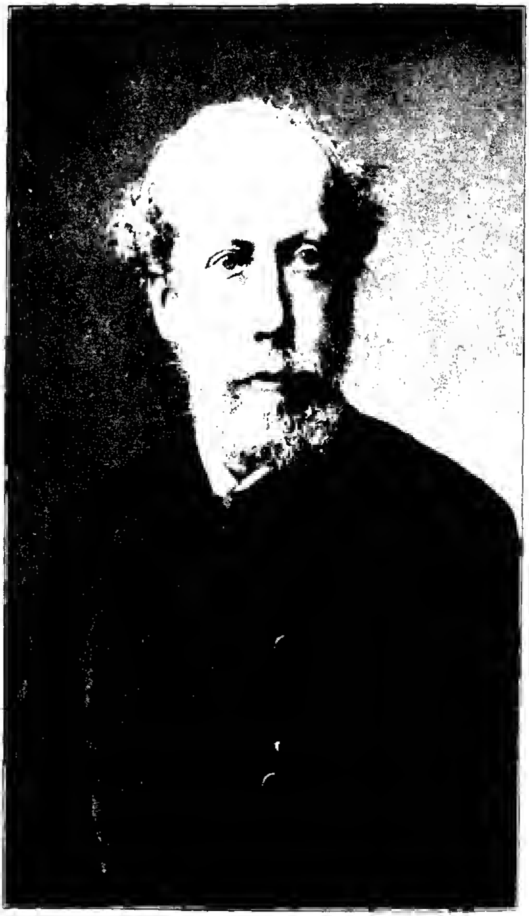
Thionyl Chloride and Silver Malate.—Four grams (a considerable excess) of silver malate suspended in 30 c.c. of ether were shaken with 1·2 grams of thionyl chloride. Sulphur dioxide was expelled from the filtered solution by passing carbon dioxide through it for twenty-four hours. The syrup which remained after distillation of the ether yielded a small quantity of crystalline product, which was washed with ether and analysed:

0·1169 gave 0·1732 CO_2 and 0·0372 H_2O. C=40·44; H=3·51.
$C_4H_4O_4$ requires C=41·38; H=3·45 per cent.

This *malic anhydride* softens below 70°, and is completely melted at 75—76°. It may be recrystallised from ether, and dissolves readily in cold water; the aqueous solution crystallises completely on evaporation in a desiccator at the ordinary temperature, yielding malic acid in an almost pure state.

The authors' thanks are due to Mr. William Dickson, who carried out a number of the above experiments, to Mr. R. Fraser Thomson for contributing an account of the preparation of bromoacetic anhydride, and to the Carnegie Trust, which has defrayed part of the cost of the investigation.

CHEMICAL RESEARCH LABORATORY,
UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD,
UNIVERSITY OF ST. ANDREWS.



LADENBURG MEMORIAL LECTURE.

DELIVERED ON OCTOBER 23RD, 1913.

BY FREDERIC STANLEY KIPPING, D.Sc., Ph.D., F.R.S.

A MEETING of this Society which is held to commemorate the life and work of a distinguished chemist is an occasion which we approach with mingled feelings. For although we have to deplore the loss of a great man, there remain with us the recollection of his high achievements, and the example of his life worthily devoted to the advancement of knowledge.

In the minds of all chemists now living, and of all those who, in the future, trace the development of the science of our time, the name of Ladenburg is, and always will be, closely associated with the chemistry of those interesting and wonderful products of nature's laboratory, the vegetable alkaloids.

The study of some of the difficult problems presented by these complex compounds formed the main part of the experimental work of the man whose memory we honour to-day. It was a task which might well have deterred the boldest and the most sanguine spirit; but by him it was faced with persistent industry and indomitable perseverance, and brought to an issue the brilliancy of which few could have foreseen. The synthesis of *dl*-coniine, followed by the resolution of the synthetic alkaloid into its optically active components, the culminating point of these researches, was perhaps the greatest of Ladenburg's successes.

It is sometimes possible to trace the steps by which an explorer of the secrets of nature has passed from one dark region to yet another even more obscure; sometimes, however, not a single footprint remains to mark the track. In Ladenburg's case, the study of the nitrogenous products of the vegetable kingdom was preceded by an investigation of the compounds of that element which dominates the mineral world; the derivatives of benzene seem to have formed the bridge by which he crossed the gulf between those two so widely different tracts, but there is no clear record of the inspiration by which he was guided. It may have been that, while searching among the musty archives of the days long past, during the preparation of his historical work on the development of chemistry, he became fascinated by the mystery surrounding the nature and the action of those potent poisons which are elaborated by plants; the product of a common weed, even such as the deadly nightshade, which could either enhance the charms of a fair lady or lead to delirium and death, might well appeal to the imagination

of the youthful chemist, and become to him an object of absorbing scientific interest.

However this may have been, the more difficult part of the task, with which I have been entrusted, is not that of tracing Ladenburg's progress as an investigator; it is that of passing in brief review the leading personal incidents of his distinguished career.

Happily, some of the difficulties ordinarily associated with such a task have in this case been dispelled by the existence of an authentic account of many of these events from his own pen. Towards the close of his life, he suffered from severe bodily ailments, which prevented him from carrying out his official duties. It was then that, at the suggestion of his friends, and as a means of intellectual recreation, he undertook the preparation of a short autobiography. A copy of this work was very kindly lent to me by Ladenburg's second son, Dr. Rudolph, and from this authoritative source most of the following particulars have been taken.

Born of Jewish parents on July 2nd, 1842, at Mannheim, in the Grand Duchy of Baden, Albert Ladenburg was one of a family of eight, of whom, however, five died quite young. Although his parents were in a good position (his father was a Rechtsanwalt), and lived in a large, many-roomed house, he and his brother and sister were brought up in the old-fashioned way, and were seldom allowed in the apartments of their father and mother.

The school to which he was sent was one in which little Latin was taught, and no Greek; one reason for this choice was that his father's experience of the classical education given at the Gymnasium had been that it took away all desire for work. From school he went on to the Polytechnicum at Karlsruhe, where he applied himself industriously to the study of mathematics, modern languages, machine construction, and other subjects, and, as he himself says, tried to make good a part of what he felt had been wanting in his earlier education.

In 1860, at eighteen years of age, he went to Heidelberg, where he attended lectures at the University, and worked very diligently at home. At first he had the idea of specialising in mathematics; but he also studied chemistry under Bunsen, and later, physics, under Kirchhoff. The lectures of Bunsen, however, proved so inspiring that Ladenburg very soon went over to chemistry, and spent the livelong day in Bunsen's laboratory. Here he met, among others, C. Graebe, H. Wichelhaus (who remained his close friend for many years), C. Liebermann, Soret, and W. Preyer. He also became acquainted with Roscoe, who often visited Bunsen in those days.

During the winter session 1862–1863, Ladenburg studied in

Berlin, attending lectures by Magnus, Ranke, and others, and in the spring of 1863 he took the Ph.D. degree at Heidelberg University, *summa cum laude*, in chemistry, physics, and mathematics.

Up to this time he had devoted himself principally to inorganic chemistry, but he now began to work with Carius, who, although *Ausserordentlicher Professor* in the University of Heidelberg, had to work in a small private laboratory outside. Here it was that Ladenburg carried out his first research work, which was on a new method of elementary organic analysis, and it was during this period that he made the acquaintance of Erlenmeyer, an acquaintance which resulted in a lasting friendship.

In the spring of 1865, Ladenburg decided to go to Ghent to work under Kekulé, who at that time was at the height of his scientific activity, and had just published his first paper on the structure of aromatic compounds. At Ghent he met Körner and Glaser, who were assistants to Kekulé; he also carried out two researches on benzene derivatives, one on the "Synthèse de l'acide anisique," the other, in conjunction with Fitz, on "Quelques derivés de l'acide paraoxybenzoique." Except for the opportunities of intercourse with Kekulé, and with the staff and students of the laboratory—opportunities which Ladenburg prized very highly—he found life in Ghent very dull, and after a short visit to London, where he met Frankland, he proceeded to Paris. Acting on Kekulé's advice, he there interviewed Berthelot, and asked for permission to become one of Berthelot's pupils; his request was granted forthwith, but when he proceeded to inquire where he should work, he was shown a large, empty room, devoid of all fittings, of which he would be the sole occupant.

Dissatisfied with the prospect of sacrificing a considerable proportion of his time in Paris to the fitting up of this room, and of having no fellow-students with whom he could converse, in order to improve his French, he obtained an introduction to Wurtz, who was professor in the Institut de chimie, and started work in his laboratory. It was there that Ladenburg met Friedel, Caventou, Naquet, A. Gautier, and others; from Wurtz's laboratory he published with Leverkus a paper "Ueber die Konstitution des Anethols."

At the beginning of the winter of 1866, after spending a few months in Germany, he went, at Friedel's invitation, to work in the École des mines, where, with Friedel, he began that important series of researches on derivatives of silicon to which reference will be made again. Shortly after the commencement of this work, he was very seriously hurt by an explosion, so seriously, in fact, that his parents, who happened to be in Paris at the time, were

hardly allowed to see him. The cause of this explosion is not mentioned in his *Lebenserinnerungen*, but judging from the work described in the first paper published by himself and Friedel, it was very probably the ignition of a mixture of the vapour of silicochloroform and air. Whatever the cause of the accident may have been, as soon as he was better, he set to work again and remained in Paris during the whole of a very hot summer, in order to make up for the days lost during his temporary disablement.

Up to this time, apparently, he had not definitely chosen a profession, but now he decided to become a teacher. To this course his father consented, although he lacked faith in his son's ability. Having consulted Bunsen and Kopp in Heidelberg on the matter of his *Habilitation*, and having been informed that the original work which he had done would be accepted, Ladenburg went for a short period to Berlin, there to undertake a projected research with Wichelhaus. This collaboration led to no definite result, but his stay in Berlin was very pleasant; it gave him an opportunity of meeting Wallach, who was assistant to Wichelhaus, and also of renewing his acquaintance with Baeyer and Martius, both of whom he had previously met in Paris. At the instance of Wichelhaus, steps were then being taken to found the *Deutsche Chemische Gesellschaft*, and both Baeyer and Martius shared with Wichelhaus this important undertaking.

In January, 1868, Ladenburg successfully underwent the ordeal of his *Habilitation*, and having spent a short time in Paris, where he continued his work with Friedel, he returned to Heidelberg, in order to rent and equip a laboratory in which he could also lecture. In those days rooms were not available in the large institute occupied by Bunsen; and Erlenmeyer, Horstmann, W. Lossen, and all the chemistry *Privatdocenten* had their own laboratories outside.

At the beginning of the term, Ladenburg commenced his first course of lectures, the subject being the history of the development of chemistry during the last hundred years. He had composed the earlier lectures while he was in Paris, and later, when continuing the task at Heidelberg, he had the advantage of the advice and criticism of Erlenmeyer. It was the matter of these lectures, carefully revised, which was published in 1869 under the title, "Vorträge über die Entwicklungsgeschichte der Chemie in den letzten hundert Jahren," a comprehensive, lucid, and critical work, which passed through several editions. At the end of his four years as *Privatdocent* in Heidelberg, he was given the title of *Professor extraordinarius*. The award of this honour, it seems, had been delayed a year, a delay which Ladenburg regarded as a punishment for his having petitioned the Ministry, on behalf of

his colleagues and himself, to provide *Privatdocenten* with laboratories suitable to their work, and to allow them to attend the University lectures at nominal fees.

In 1872, he accepted, after some hesitation, the offer of the chair of chemistry in the University of Kiel. The prospects there were not attractive. On his first visit, the town itself, the University, and some of the public buildings, gave him the impression of wretchedness, an impression, however, which was afterwards modified. There was, moreover, no chemistry department; and although it was understood that one should be built and equipped in about three years, there was no place in which he could work in the meantime. Nevertheless, he finally decided to accept the professorship, and in 1873 he began to teach at Kiel in a temporary laboratory, which had been rapidly fitted up in a vacant dwelling house.

At first he had only a few students, and could give much time to his own work, although he was worried by frequently occurring committee meetings, at which there were long and acrimonious disputes among the professors, each of whom was eager to secure the best site for his own projected buildings. During this period of comparative freedom from his teaching duties, he was able to commence, in conjunction with various other chemists, the preparation of his "Handwörterbuch der Chemie," a work which was finally pubished in thirteen royal octavo volumes.

The new Chemistry Institute in Kiel, of which Ladenburg was appointed Rector in 1884, was not ready for occupation until the winter session of 1878–1879. Attracted by the fame of the professor, and by the lucidity and fire of his lectures, students came in rapidly increasing numbers, and soon his laboratory became crowded. While at Kiel he was responsible for passing more than twenty-five doctors of philosophy in chemistry, and it was there that he carried out many of his more important researches on the alkaloids, including the synthesis of coniine. Towards the end of his stay in Kiel, he suffered a very severe blow in the loss of his mother, to whom he was deeply attached.

In 1889, he was offered the professorship of chemistry in the University of Breslau. At first he decided to decline the call, as he found, on visiting the town, that it was devoid of all attractions, while the so-called laboratory was hardly worthy to be dignified by such a name. However, having obtained a promise that the buildings then in use should be immediately reconstructed, and that a large new Institute should very soon be erected, he accepted the chair, and took up his residence in Breslau.

At first he was very disappointed that only twenty-five students

came to work with him, and that his lectures were only very sparsely attended, but as time went on, and especially after the new Institute had been opened in 1897, the number of his students increased to such an extent that on his resignation of the chair in 1909, he had the satisfaction of having passed 160 doctors of philosophy in chemistry. Few could show such a splendid record, even in those days, when the stream of prospective German chemists was at its flood.

During his first twelve years at Breslau nothing occurred to diminish Ladenburg's mental or bodily activity, but from 1901 onwards, one great trouble quickly succeeded another. He lost his youngest son, who had been ill for many years; his relations with friends and colleagues were sorely embittered by a controversy arising out of an address entitled "Einfluss der Naturwissenschaften auf die Weltanschauung," delivered at the *Naturforscherversammlung* in Kassel in 1903; and in 1904 he himself became ill, and shortly afterwards had to undergo a serious operation. Although, after many months of suffering, he recovered sufficiently to be able to resume fitfully his academic duties, his health soon gave way again. The tragic loss of his eldest son, who was drowned in 1908; the death of his wife, after a most distressing illness; and his own serious ailments, led him in 1909 to tender his resignation. He died two years later, on August 15th, 1911, in his seventieth year.

A man, like Ladenburg, who, in spite of poor health, leaves a record so deeply graven on the roll of fame, must have been possessed of inexhaustible and indomitable will-power and untiring industry. Even as a youth, his devotion to his work led him to refuse the delights of a long tour in Switzerland in order to spend the time in Bunsen's laboratory; and it was by this spirit that the whole of his life was ruled.

The honours which were bestowed on him and which were earned by this stern self-sacrifice on the altar of science, were not confined to those which he received in Germany; for in addition to the title of *geheimer Regierungsrath*, the Rectorship of the University of Kiel, and the membership of the *Akademie der Wissenschaften* of Berlin, he was an Honorary and Foreign Member of this Society, a member of the *Académie des Sciences*, and correspondent for the chemistry sections of numerous other scientific societies; he was awarded the Hanbury Medal of the Pharmaceutical Society in 1902, and the Davy Medal of the Royal Society in 1907.

Well might these honours and the place which he had gained for himself in the scientific world afford him some consolation in the dark days of his closing years; but possibly they seemed to him of

little import in comparison with the glad memories of more than thirty years of happy wedded life.

His wife was Margarete, the eldest daughter of Pringsheim, professor of botany in the University of Berlin. He met her late in 1875, during a visit to the capital, and with him it was a case of love at first sight; he proposed the following Easter, and they were married on September 19th of the same year. They had three sons, of whom only one survives.

Except when writing of his relations and friends, for whom he expresses freely his deep love and affection, Ladenburg preserves in his recollections a dignified silence as to his own feelings, and a reserved modesty as to his own achievements. He does not even refer to his great "Handwörterbuch der Chemie," the completion of which must have given him profound satisfaction; nor is there a word to intimate the acute intellectual gratification which he must have felt when he had brought some important research to a successful issue. To a man of his devotion to science, however, the joy of adding a store to the eternal edifice of truth must have been intense; and, though unrecorded, his feelings when he first glanced through the polarimeter tube containing his synthetic optically active coniine, might perhaps have been expressed in the words which Biot once addressed to Pasteur: "J'ai tant aimé les sciences dans ma vie, que cela me fait battre le cœur."

However great may have been Ladenburg's own satisfaction on that occasion, he hastened to share it with his wife, who happened to be away from Kiel at the time; the brief telegram, "Gretchen, es dreht," which he sent to her,* conveyed no doubt infinitely more than was expressed in those three words.

In spite of the reticence as to his own characteristics which pervades his *Lebenserinnerungen*, there are a few passages which throw dim sidelights on his personality. He was the kind of man we call resolute or stubborn, strong-willed or obstinate, according as his point of view agrees or disagrees with our own. When he felt himself in the right, he defended his position tenaciously, a course which involved him in litigation on more than one occasion, and which led him to publish a considerable number of polemical papers.

The unremitting attention which he gave to his academic duties left him but little time for relaxation; nevertheless, like so many of his race, he possessed musical talent of a high order, and cultivated this gift in his rare moments of leisure. In his early youth at Karlsruhe, he spent many hours at the piano; later at Heidelberg he played in quartets and other concerted music, and obtained

* Dr. Rudolf Ladenburg kindly gave me this information.—F. S. K.

a great mastery over his instrument. He was a great lover of Brahms, with whose compositions he had been made familiar by Frau Schumann, a frequent visitor at his father's house and his own. He would travel a long distance in order to hear a new work of this composer, and when at Kiel he considered it his duty to cultivate among his friends a taste for Brahms, whose music at that time was little known in the town. On several occasions he met Brahms, and had the intense pleasure of hearing that great genius interpret his own compositions.

This brief outline of Ladenburg's life, drawn by one who had not the honour of his acquaintance, must necessarily fail completely to give a picture of the living man. As this defect could not be remedied, the delineation of Ladenburg's character may be left to the more competent pen of one of his own countrymen and colleagues, the writer of the memorial published in the *Berichte*.

When in 1866 Ladenburg was invited by Friedel to go and work in Paris on compounds of silicon, only a few organic derivatives of that element were known; those containing a silicon atom directly united to a carbon atom could, in fact, be counted on the fingers of one hand. If this state of knowledge is contrasted with that which obtained in 1883, when Beilstein's "Handbuch der organischen Chemie" was first published, some idea may be gained of the progress which had been made during the intervening years. This great advance was principally due to those researches which, commenced with Friedel, were continued by Ladenburg alone, and which formed, not the very first, but one of the earlier chapters of the latter's scientific record.

The first joint communication, published in 1867 (*Annalen*, **143**, 118), contained an account of silicochloroform. Some ten years previously Buff and Wöhler had heated crystalline silicon in a stream of dry hydrogen chloride, and had obtained a liquid to which they had given the formula $Si_2Cl_3 + 2HCl$ ($Si=21$); this formula was subsequently altered by Wöhler to $Si_6Cl_{10}H_4$ ($Si=14$), but he recognised the fact that he had been unable to obtain the liquid in a pure state, and that consequently its formula was not definitely established. Friedel and Ladenburg prepared this compound in a state of purity, and proved it to have the molecular formula $SiHCl_3$; its further study led them to the discovery of several interesting and novel reactions. One of its derivatives, namely, triethyl orthosilicoformate, which was obtained by treating the trichloro compound with ethyl alcohol, underwent a remarkable decomposition when it was warmed with sodium: the metal remained unchanged, but the ester was decomposed, giving pure silicomethane, SiH_4, and

an ester of orthosilicic acid, a change which is expressed by the following equation: $4SiH(OEt)_3 = SiH_4 + 3Si(OEt)_4$.

This reaction, which is comparable to the decomposition by heat of the lower acids of phosphorus into phosphine and orthophosphoric acid, passed into the text-books of inorganic chemistry as a method for the preparation of pure silicomethane, and the equation just given has certainly been committed to memory, for examination purposes, by many puzzled students, who had not the remotest idea of the nature of triethyl orthosilicoformate.

As silicomethane had not until then been prepared in a pure state, Friedel and Ladenburg established its composition, and found that the pure gas was not spontaneously inflammable in air at the ordinary temperature and pressure, but was so under lower pressures. In addition to silicochloroform, they investigated other purely inorganic silicon compounds, more particularly silicon oxychloride, $SiCl_3 \cdot O \cdot SiCl_3$, which they prepared by passing the vapour of silicon tetrachloride through a white hot porcelain tube (*Ber.*, 1868, **1**, 86); although unable to discover how this compound was produced, they proved that it reacted with alcohol, giving the ethoxy-derivative, $Si(OEt)_3 \cdot O \cdot Si(OEt)_3$, and with zinc ethyl at 180°, giving silicoethyl oxide, $SiEt_3 \cdot O \cdot SiEt_3$.

The only method available in those days for bringing about the direct union of silicon and carbon was to heat silicon tetrachloride with zinc alkyls in sealed tubes. By using sodium in conjunction with the zinc compound, Friedel and Ladenburg succeeded in bringing about the displacement of the chlorine by an alkyl group at much lower temperatures and without the use of sealed tubes (*Ber.*, 1870, **3**, 15). In this way they prepared triethyl orthosilicopropionate, $SiEt(OEt)_3$, from triethoxysilicic chloride, which was itself obtained by the interaction of silicon tetrachloride and ethyl alcohol.

This ester was not completely hydrolysed by alcoholic potash in the cold, and when boiled with a concentrated aqueous solution of the alkali, it gave a product which had only approximately the composition $EtSiO \cdot OH$. For the preparation of the pure acid the ester was heated in sealed tubes with acetic chloride, and the product, ethylsilicon trichloride, $SiEtCl_3$, was hydrolysed with water. Silicopropionic acid, $EtSiO \cdot OH$, was thus obtained as an amorphous powder; it was the first representative of the silicon analogues of the carboxylic acids. Although, later on, Ladenburg prepared silicoacetic acid, $MeSiO \cdot OH$ (*Ber.*, 1873, **6**, 1029), and silicobenzoic acid, $PhSiO \cdot OH$, and several compounds supposed to be of this type have been obtained in recent times, little is known of their nature: except for the fact that such acids give soluble potassium salts,

they are extremely inert, and behave in every respect differently from the carboxylic acids.

The discovery of silicopropionic acid raised in Ladenburg's mind a question which, some years afterwards, he attempted to solve (*Ber.*, 1872, **5**, 568), namely, whether the silicon which is contained in plants is in combination with carbon or is a constituent of a purely mineral silicate. This problem, apparently, is still awaiting solution.

The main object of the joint researches just referred to was to gain some information as to the extent of the analogy between compounds of silicon and carbon; to ascertain whether the new theories which were just then being developed in connexion with organic compounds could also be applied to the so-called inorganic elements, or whether, as some believed, these new theories were both "unnütz und verwirrend."

As a further step in this direction, Friedel and Ladenburg (*Bull. Soc. chim.*, 1867, [ii], **7**, 65) attempted the synthesis of a quaternary hydrocarbon, and succeeded in obtaining dimethyldiethylmethane, CMe_2Et_2, the first known compound of this type; the existence of this hydrocarbon proved that the carbon atom, like the silicon atom in Friedel and Craft's tetraethylsilicane, $SiEt_4$, could unite directly with four hydrocarbon radicles.

They next tried to obtain a compound in the molecule of which two silicon atoms were directly united, as are the carbon atoms in ethane; after many fruitless attempts they finally succeeded (*Bull. Soc. chim.*, 1869, [ii], **12**, 92; *Annalen*, 1880, **203**, 241) in preparing silicoethane, $SiEt_3{\cdot}SiEt_3$, in the following manner: Silicon tetraiodide was heated with molecular silver at about 300°, and was thus converted into the hexaiodide, Si_2I_6 (from which the corresponding bromide, Si_2Br_6, and chloride, Si_2Cl_6, were prepared). The hexaiodide was hydrolysed with ice-cold water, yielding an amorphous product, silico-oxalic acid, $\begin{array}{l}SiO{\cdot}OH\\|\\SiO{\cdot}OH\end{array}$, which showed an interesting behaviour; when heated in the air, the acid was decomposed into silica and hydrogen; when warmed with potassium hydroxide it gave potassium metasilicate with evolution of hydrogen:

$$H_2SiO_4 + 4KOH = 2K_2SiO_3 + 2H_2O + H_2.$$

The interaction of silicon hexaiodide and zinc ethyl took place very readily, giving a colourless liquid, boiling at 250—253°, which was proved to be the desired compound, hexaethylsilicoethane, $SiEt_3{\cdot}SiEt_3$.

During the preparation of triethyl silicoformate from triethylsilicic chloride, Friedel and Ladenburg had observed the formation

of diethoxydiethylsilicane, $SiEt_2(OEt)_2$, as a by-product. This observation led Ladenburg to study the action of zinc ethyl and sodium on ethyl orthosilicate, $Si(OEt)_4$. In a series of papers (*Ber.*, 1871, **4**, 727, 901; 1872, **5**, 565, 1081) he showed that the ethoxy-groups in this ester might be successively displaced by ethyl radicles, giving the compounds $SiEt(OEt)_3$, $SiEt_2(OEt)_2$, $SiEt_3{\cdot}OEt$, and $SiEt_4$, as well as triethylsilicane, $SiEt_3H$.

The diethoxydiethyl derivative, $SiEt_2(OEt)_2$, could not be hydrolysed to the corresponding dihydroxy-compound with alcoholic potash, but when heated with acetyl chloride in sealed tubes it gave the halogen derivatives $SiEt_2(OEt)Cl$ and $SiEt_2Cl_2$; the latter, with water, yielded a thick syrup, which Ladenburg regarded as silicon diethyl ketone, or oxide, $SiEt_2O$, but the analytical results did not agree well with those required for this formula.

The monoethoxy-derivative was hydrolysed by hydriodic acid, but gave the oxide $SiEt_3{\cdot}O{\cdot}SiEt_3$; when heated at 180° with acetyl chloride, it was converted into silicoheptyl chloride, $SiEt_3Cl$, which, with ammonia, gave silicoheptyl alcohol, $SiEt_3{\cdot}OH$. This was the first known silicon derivative of the alcohol type, and for this and analogous compounds, Ladenburg proposed the class name "silicole," corresponding with Kolbe's "carbinole."

A few silicon derivatives containing aromatic radicles were also prepared, as, for example, phenylsilicon trichloride, $SiPhCl_3$, which was obtained by heating silicon tetrachloride with mercuric phenyl (*Ber.*, 1873, **6**, 379). This trichloride and the ester, $SiPh(OEt)_3$, prepared from it, gave on hydrolysis products which seemed to be identical, and which were believed to be silicobenzoic acid, $PhSiO{\cdot}OH$.

Some thirty years later Ladenburg's thoughts again turned to these aromatic silicon compounds, and he prepared various derivatives of silicon tetraphenyl (*Ber.*, 1907, **40**, 2274), but apparently his attempts to sulphonate triphenylsilicol were not successful (*Ber.*, 1908, **41**, 966).

This short summary of Ladenburg's researches on silicon compounds can give little idea of the very great experimental difficulties with which he had to contend, and of the time which he must have devoted to these investigations. But in spite of the exacting character of this work, during its progress he was also able to study some organic compounds of tin.

The object here was not, as might have been expected, to establish some analogy between tin and silicon; it was to try and find out whether the molecule of a stannous compound contained one or two atoms of tin. In his opinion, the *ous* compounds of iron, manganese, chromium, and other metals contained two atoms of the

metal in their molecules (*Ber.*, 1869, **2**, 706), but experiments with certain inorganic iron, manganese, and tin compounds failed to give any evidence in support of this view. He therefore prepared "stanntriäthyl," a compound which had been obtained by Cahours, but the formula of which had not been established. This ethyl derivative was proved to have the composition, Sn_2Et_6, and the fact that two atoms of tin could unite directly was thus established, although the molecular structure of stannous compounds still remained unknown (*Ber.*, 1870, **3**, 353).

From the hexaethyl derivative Ladenburg prepared various other organic tin compounds; he showed that it was decomposed by iodine, giving tin triethyl iodide, $SnEt_3I$, from which, with the aid of sodium and bromobenzene, he obtained tin phenyltriethyl, $SnEt_3Ph$ (*Ber.*, 1871, **4**, 17). He also found (*Ber.*, 1871, **4**, 19) that the hexaethyl compound underwent the following interesting decompositions:

$$Sn_2Et_6 + 2EtI = 2SnEt_3I + C_4H_{10}.$$

$$Sn_2Et_6 + 2CH_2Cl{\cdot}CO_2H = 2SnEt_2Cl_2 + 2CO_2 + 2C_2H_6 + C_4H_{10}.$$

A much more important chapter of Ladenburg's work is that containing his numerous contributions, both theoretical and practical, on benzene and its derivatives. That a young and enthusiastic chemist, who had worked in Kekulé's laboratory, would take an active part in the solution of the many interesting problems suggested by the theory of the structure of benzene was, of course, only to be expected; it was merely a question of how far his own efforts would meet with success.

As a matter of fact, of the many who assisted in the examination of the fundamental propositions of the aromatic theory, few played a more prominent part than Ladenburg, or brought perspicacity and critical acumen of a higher order to the discussion of the experimental data. His first researches on aromatic compounds, carried out in Kekulé's laboratory and published in 1866–1867, have already been mentioned. During the next two years, although fully occupied with silicon compounds in the laboratory, his mind was evidently running on the aromatic theory, and as early as 1869 he contributed a paper in which he had the temerity to criticise Kekulé's formula, and to suggest alternatives, among which occurred the now well-known prism formula, originally put forward by Claus.

In this paper (*Ber.*, 1869, **2**, 272) Ladenburg showed that whereas, according to Kekulé's formula, the positions 1 : 2 and 1 : 6 must be, and the positions 1 : 3 and 1 : 5 may be, different, certain experimental data of Hübner and Petermann pointed strongly to the contrary conclusion, namely, that in the benzene

nucleus there are two hydrogen atoms which are symmetrically situated with respect to a third such atom. The argument was as follows: *m*-Bromobenzoic acid gives two bromonitrobenzoic acids, which, on reduction, are converted into the same aminobenzoic acid. The nitro-groups in the bromonitro-acids must have displaced two hydrogen atoms, which are differently situated with regard to the bromine atom, but identically situated with respect to the carboxyl group. Therefore either the position 1 : 2 = 1 : 6, or 1 : 3 = 1 : 5.

A few years later (*Ber.*, 1872, **5**, 322) he discussed the isomerism of benzene derivatives. The view that only three di-substitution products could be obtained was at that time supported by negative evidence only; no more than three such isomeric compounds had ever been prepared. From data established by Carstanjen (*J. pr. Chem.*, 1871, [ii], **3**, 50) in an experimental investigation of hydroxythymoquinone, Ladenburg not only deduced important conclusions regarding the symmetry of the benzene molecule, but also argued from Carstanjen's facts that only three di-substitution products of benzene were theoretically possible.

Two papers on pentachlorobenzene (*Ber.*, 1872, **5**, 789; 1873, **6**, 32) may next be mentioned, as they illustrate the experimental skill with which Ladenburg overcame a very difficult practical problem.

Two pentachlorobenzenes had been described, the one by Otto, the other by Jungfleisch. As the result of a most laborious investigation, involving hundreds of fractional crystallisations (*Annalen*, 1874, **172**, 331), Ladenburg was able to show that the supposed isomerides did not exist, and that a statement which could not be reconciled with the "Gleichwertigkeit" of the six hydrogen atoms of benzene had no foundation in fact.

In his work on mesitylene, which was published shortly afterwards (*Ber.*, 1874, **7**, 1133; *Annalen*, 1875, **179**, 163), he proved that the three displaceable hydrogen atoms in this hydrocarbon were all "gleichwertig," and consequently that mesitylene was symmetrical trimethylbenzene.

The proof was as follows: Dinitromesitylene, which may be represented by the formula $C_6Me_3\overset{a}{H}\overset{b}{NO_2}\overset{c}{NO_2}$, was converted into nitromesidine, $C_6Me_3\overset{a}{H}\overset{b}{NO_2}\overset{c}{NH_2}$, by reduction, and the acetyl derivative of this base was transformed into dinitracetmesidine, $C_6Me_3\overset{a}{NO_2}\overset{b}{NO_2}\overset{c}{NHAc}$. This compound was hydrolysed, and the dinitroamino-derivative converted into a dinitromesitylene, $C_6Me_3\overset{a}{NO_2}\overset{b}{NO_2}\overset{c}{H}$, by Griess' method. The substance thus obtained

was identical with the original dinitromesitylene; therefore two of the displaceable hydrogen atoms, *a* and *c*, are "gleichwertig."

The nitromesidine, $C_6Me_3\overset{a}{H}\overset{b}{NO_2}\overset{c}{NH_2}$, obtained from the dinitromesitylene, $C_6Me_3\overset{a}{H}\overset{b}{NO_2}\overset{c}{NO_2}$, gave the mononitro-derivative, $C_6Me_3\overset{a}{H}\overset{b}{NO_2}\overset{c}{H}$, when the amino-group was displaced by hydrogen. The nitro-compound was then reduced to mesidine, acetylmesidine was nitrated, and the product was hydrolysed to a nitromesidine, $C_6Me_3\overset{a}{NO_2}\overset{b}{NH_2}\overset{c}{H}$, or $C_6Me_3\overset{a}{H}\overset{b}{NH_2}\overset{c}{NO_2}$; but since $a=c$, these formulæ are identical. Since, moreover, this nitromesidine was identical with that, $C_6Me_3\overset{a}{H}\overset{b}{NO_2}\overset{c}{NH_2}$, obtained from dinitromesitylene, $b=c$, and therefore $a=b=c$. He frankly recognised that the fact that mesitylene was symmetrical trimethylbenzene afforded strong evidence against the prism formula, and he concluded therefore that "there is at the present time no symbolic representation of benzene which satisfies all requirements."

Another paper which has become a classic is that in which Ladenburg showed that in the benzene nucleus there were at least four hydrogen atoms which were identically situated (*Ber.*, 1874, **7**, 1684). His proof, which is of such fundamental importance that it is given in most of the text-books of organic chemistry, was the following. Phenol, treated with phosphorus pentabromide, gave bromobenzene, from which, with the aid of sodium and carbon dioxide, benzoic acid was obtained. Now benzoic acid was known to give rise to three isomeric hydroxybenzoic acids, $C_6H_4(OH)\cdot CO_2H$; in each of these compounds the hydroxyl group must have displaced a different hydrogen atom from the benzene nucleus, and none of these hydrogen atoms was identical with that displaced by the hydroxyl group in the original phenol. All three hydroxybenzoic acids were converted into a phenol and carbon dioxide: the phenol thus obtained was in every case identical with the original compound.

The substance of Ladenburg's more important contributions to the chemistry of benzene is to be found in his "Theorie der aromatischen Verbindungen," published in 1876, a few years after he went to Kiel. In this monograph he gave a critical review of the position of the aromatic theory at that time, and also did a great service to chemistry by drawing attention to the importance of Körner's method for the orientation of benzene derivatives.

Various other researches on aromatic compounds, including those on the aldehydine bases (*Ber.*, 1878, **11**, 590, 1648; see also *Ber.*, 1878, **11**, 1653, 1656), were carried out between 1876 and 1878,

but in the following year he began his study of the alkaloids and related compounds, a task which, with its side issues, occupied him almost exclusively during the rest of his working life.

In those days there were known various vegetable products, which were used in medicine for different purposes, but had in common the remarkable property of dilating the pupil of the eye. Among these alkaloids were belladonine and atropine, obtained from the deadly nightshade (*Atropa belladonna*), henbane, or hyoscyamine, from *Hyoscyamus niger*, duboisine, from *Duboisia myoporoides*, and daturine, from *Datura strammonium*. The only one of these substances that had been investigated other than very superficially was atropine; Lossen had shown that this base was hydrolysed by concentrated hydrochloric acid, giving tropine and tropic acid:

$$C_{17}H_{23}O_3N + H_2O = C_8H_{15}ON + C_9H_{10}O_3;$$

from tropic acid, atropic acid, $C_9H_8O_2$ (and isatropic acid) had been obtained, and atropic acid had been reduced to hydratropic acid, $C_9H_{10}O_2$.

Ladenburg first succeeded in preparing atropine from its decomposition products by evaporating a dilute hydrochloric acid solution of tropine with tropic acid (*Ber.*, 1879, **12**, 941); he found that this artificial atropine was identical with the natural product in every respect, including its physiological action.

He then showed that tropine reacted with other organic acids in a similar manner, in presence of hydrochloric acid, giving compounds which he named tropeines (*Ber.*, 1880, **13**, 1081; 1882, **15**, 1025); of these, the product from tropine and mandelic acid, phenylglycolyltropeine, or homatropine, $C_{16}H_{21}O_3N$, had a mydriatic action not quite so strong as, but much more rapid than, that of atropine; homatropine, moreover, was less poisonous than atropine. This partially synthetic alkaloid found application in ophthalmic surgery.

The results of the further investigation of atropine were published in numerous papers during 1880–1882, and were briefly as follows: Hydratropic acid, $C_6H_5\cdot CHMe\cdot CO_2H$, oxidised with permanganate (Ladenburg and Rügheimer, *Ber.*, 1880, **13**, 373), gave an acid, $C_9H_{10}O_3$, which was identical with the atrolactinic acid obtained by Fittig and Wurster (*Annalen*, 1879, **195**, 145) by treating atropic acid with hydrobromic acid and hydrolysing the product; this fact showed that atrolactinic acid had not the constitution $C_6H_5\cdot CH(CH_2\cdot OH)\cdot CO_2H$ assigned to it by Fittig and Wurster, but $C_6H_5\cdot C(OH)(CH_3)\cdot CO_2H$. Atrolactinic acid, heated with hydrochloric acid, was converted into atropic acid; the latter

combined with hypochlorous acid to form a chlorohydroxy-acid, from which tropic acid was obtained when the chlorine was displaced by hydrogen.

These results showed that tropic acid was not

$$C_6H_5\cdot C(OH)(CH_3)\cdot CO_2H,$$

as suggested by Fittig and Wurster, and that the relationship between the four acids just mentioned was as follows:

$C_6H_5\cdot CH<{}^{CH_3}_{CO_2H}$	$C_6H_5\cdot C(OH)<{}^{CH_3}_{CO_2H}$
(I.) Hydratropic acid.	(II.) Atrolactinic acid.
$C_6H_5\cdot C\leqslant{}^{CH_2}_{CO_2H}$	$C_6H_5\cdot CH<{}^{CH_2\cdot OH}_{CO_2H}$
(III.) Atropic acid.	(IV.) Tropic acid.

The synthesis of tropic acid was then accomplished in conjunction with Rügheimer (*Ber.*, 1880, **13**, 2041). Acetophenone dichloride, boiled with potassium cyanide in alcoholic solution, gave the compound $C_6H_5\cdot CMe(OEt)\cdot CN$, which, on hydrolysis, was converted into the acid $C_6H_5\cdot CMe(OEt)\cdot CO_2H$; the latter, with concentrated hydrochloric acid, gave atropic acid (III), from which tropic acid was prepared in the manner described above.

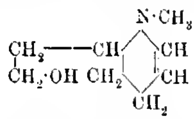
The determination of the constitution of tropine, the other decomposition product of atropine, was a much more difficult task, which Ladenburg attacked with great vigour. He found that when tropine, $C_8H_{15}ON$, was heated with concentrated hydrochloric acid, it was converted into tropidine, $C_8H_{13}N$ (*Ber.*, 1879, **12**, 944; 1880, **13**, 252); when heated with hydriodic acid, it gave an iodide, $C_8H_{15}NI_2$ (*Ber.*, 1881, **14**, 227), which, on reduction with zinc and hydrochloric acid, yielded hydrotropidine, $C_8H_{15}N$ (*Ber.*, 1883, **16**, 1408). When distilled with soda-lime, tropine gave methylamine, trimethylamine, hydrogen, and a hydrocarbon which was suspected to be valerylene, but its nature was not established (*Ber.*, 1881, **14**, 227).

As these results seemed to indicate that tropine was a derivative of a reduced pyridine or an oxidised piperidine nucleus, he prepared various alkylpiperidine derivatives, among others, *N*-propyl- and *N*-*iso*propyl-piperidine, and tried to convert these compounds by oxidation and other means into a base, which might prove to be identical with tropine or tropidine (*Ber.*, 1881, **14**, 1342). These experiments having failed, and the degradation of tropine by distillation with soda-lime having given such poor results, he next applied to this base a method which had been recently discovered by Hofmann, the now well-known process of exhaustive methylation.

From tropine and methyl iodide he obtained an iodide of methyltropine, $C_9H_{17}ON$, and found that this base was decomposed by

potassium hydroxide, giving dimethylamine (*Ber.*, 1881, **14**, 2126). Methyltropine, on further methylation, gave dimethyltropine iodide, from which by distillation, he obtained trimethylamine, an oil, $C_7H_{10}O$, which he named *tropilene*, and a hydrocarbon of the composition C_7H_8, which he called *tropilidene* (*Ber.*, 1881, **14**, 2403); this hydrocarbon seemed to be identical with that which he had previously obtained from tropine.

The composition and properties of tropilene led Ladenburg to conclude that this compound was related to suberone; he oxidised it with nitric acid, and found that it gave an acid which was probably normal adipic acid (*Ber.*, 1882, **15**, 1028). At the same time he discovered another very important fact, namely, that tropidine hydrobromide, heated with bromine at 170—180°, gave ethylene dibromide and dibromomethylpyridine; with excess of bromine it gave ethylene dibromide and dibromopyridine (*Ber.*, 1882, **15**, 1140). From all these observations he concluded that tropine was probably a methylpiperidine or methylpyridine derivative of the following constitution (*Ber.*, 1882, **15**, 1028):



While these experiments were in progress he also examined several of the other mydriatic drugs; in the course of this work he showed that duboisine and daturine were probably identical with hyoscyamine, that belladonine probably contained atropine, and that hyoscyamine and atropine were very closely related, so closely, in fact, that atropine could be synthesised from the decomposition products of hyoscyamine.

About 1882, Ladenburg's direct study of these mydriatic alkaloids gave place to his synthetic work on piperidine and pyridine derivatives. The main object of these researches was, no doubt, the synthesis of tropine, since he thought that this base was related to pyridine in the manner shown above.

The first important step in these synthetical experiments was the discovery that pentamethylenediamine could be obtained by the reduction of trimethylene dicyanide with zinc and hydrochloric acid (*Ber.*, 1883, **16**, 1149). This base, heated with sodium hydroxide, gave a compound, $C_5H_{11}N$, which seemed to be piperidine, and the identity of the synthetic base with that obtained from pepper was fully established by Ladenburg and Roth (*Ber.*, 1884, **17**, 513). As the yield of pentamethylenediamine in the above process was very unsatisfactory, Ladenburg devised a better

method for the preparation of the base, which consisted in reducing the dicyanide with sodium and alcohol (*Ber.*, 1885, **18**, 2956); he also showed that the hydrochloride of the diamine was converted into piperidine and ammonium chloride when it was distilled; as this change was evidently no far-reaching decomposition, the synthesis of piperidine in this way established the constitutional formula at that time assigned to that base.

While this synthesis of piperidine was in progress, he studied the behaviour of pyridine ethiodide at high temperatures (*Ber.*, 1883, **16**, 1410), and found that it gave ethylpyridine hydriodide when it was heated, by intramolecular change, just as the *N*-substituted anilines were known to give homologues of that base (Hofmann). He proved that the product contained γ-ethylpyridine by oxidising a fraction of it to *iso*nicotinic acid (*Ber.*, 1883, **16**, 2059), and also showed later (*Ber.*, 1885, **18**, 2961) that α-ethylpyridine and αγ-diethylpyridine were also produced, together with the γ-ethyl derivative, when pyridine ethiodide was heated.

It was now possible to obtain derivatives of pyridine from that base itself; in order to convert these compounds into the corresponding piperidine derivatives, Ladenburg investigated a method described by König for the reduction of pyridine to piperidine with zinc and hydrochloric acid, but he was unable to obtain any piperidine. He next tried reduction with sodium and alcohol, a process used by Wischnegradsky, and by a suitable improvement of this method, he was able to reduce coal tar picoline almost completely. In this way he obtained α-methylpiperidine, mixed with the β-compound, the first homologues of piperidine, excluding the *N*-derivatives, which had been prepared (*Ber.*, 1884, **17**, 388). He also reduced his γ-ethylpyridine to the piperidine derivative, and found that the latter had an odour of coniine.

This observation and the results of Hofmann's work, which had shown that coniine was in all probability α-propylpiperidine, led Ladenburg to attempt the synthesis of the last-named compound. With this end in view, he heated pyridine propiodide, and obtained a mixture of bases: one of these compounds gave, on oxidation, pyridine-γ-carboxylic acid, and seemed to be γ-propylpyridine: the other could not be obtained in a state of purity. The pure and the impure isomerides were separately reduced to piperidine derivatives: these compounds resembled coniine, but neither was identical with the latter. Immediately afterwards, with Schrade, he prepared α- and γ-*iso*propylpyridine in a similar manner from pyridine *iso*propiodide (*Ber.*, 1884, **17**, 1121). As these two compounds, like the supposed propyl derivatives, could not be completely separated by distillation, he converted the crude bases into the

corresponding piperidine derivatives by reduction with sodium and alcohol (*Ber.*, 1884, **17**, 1676), and then purified the latter with the aid of their platinichlorides.

The α-*iso*propylpiperidine thus obtained in a pure condition was carefully compared with coniine, and found to be remarkably similar to that base in all its properties, including its physiological action; the observed differences might be due merely to the optical inactivity of the synthetical base.

It was then found (*Ber.*, 1885, **18**, 1587) that the α- and γ-*iso*propylpyridines and also the supposed corresponding propyl derivatives could be completely purified with the aid of their platinichlorides; in each case the base of lower boiling point gave on oxidation picolinic acid, and was therefore the α derivative, whilst the isomeride gave *iso*nicotinic acid, and was therefore the γ-derivative.

The pure α-pyridine bases (propyl and *iso*propyl) were carefully compared with conyrine, which Hofmann had obtained by heating coniine hydrochloride with zinc dust, and had shown to be either α-propyl or α-*iso*propylpyridine. They both differed from conyrine. Therefore, either the difference was merely due to stereoisomerism, or else the two synthetical bases must both be *iso*propylpyridine. The latter alternative was proved to be the true one; when pyridine propiodide was heated in order to convert it into propylpyridine, the *n*-propyl was transformed into the *iso*propyl group.

Since it had thus been proved that conyrine must be α-propylpyridine, Ladenburg attempted to prepare this base from pyridine allyl iodide, but obtained *iso*propylpyridine in place of the desired propyl compound (*Ber.*, 1885, **18**, 1587). Next he tried to condense picoline with paracetaldehyde in the presence of zinc chloride (*Ber.*, 1886, **19**, 439), a reaction which Jacobsen and Reimer had applied to obtain benzylidenequinaldine from quinaldine and benzaldehyde. In this way he obtained only very small quantities of an oily base, but the product had an odour of conyrine, and on analysis seemed to be allylpyridine. On reduction with sodium and alcohol, it gave a base having properties similar to those of coniine. These experiments were repeated with larger quantities of material (*Ber.*, 1886, **19**, 2578); 380 grams of picoline were treated in sealed tubes, and 45 grams of allylpyridine were obtained; the product was proved to be the α-derivative by oxidising it to picolinic acid, and was reduced to propylpiperidine; the latter was oxidised by Hofmann's method (*Ber.*, 1884, **17**, 825) to a base, which was found to be identical with conyrine. The synthetical propylpiperidine was finally converted into the acid tartrate, and the solution of the latter was seeded with a crystal of coniine acid tartrate; the crystal-

line deposit was decomposed with potassium hydroxide, and the liberated base was found to be dextrorotatory. The complete identity of the synthetical base with coniine, obtained from the hemlock, was then fully established; the alkaloid which had caused the death of the wisest of men was the first to succumb to the synthetic skill of the chemist!

This synthesis of coniine was accomplished in 1886, and for nearly twenty years afterwards Ladenburg continued his researches with undiminished activity. During this period he was occupied to a great extent with various issues arising out of his earlier work; it will therefore be more convenient to deal with the discoveries of this period under certain definite headings rather than to consider them in strict chronological sequence.

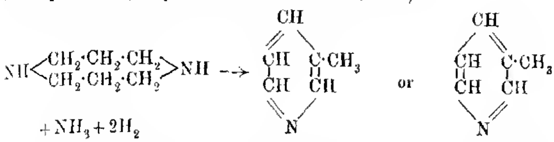
His studies of the diamines may be first considered (*Ber.*, 1886, **19**, 2585). He showed that his synthetical pentamethylenediamine was identical with cadaverine, a base isolated by Brieger from putrefying flesh. Tetramethylenediamine (*Ber.*, 1886, **19**, 780; 1887, **20**, 442) was converted into pyrrolidine, $\begin{matrix} CH_2\cdot CH_2 \\ | \\ CH_2\cdot CH_2 \end{matrix}\!\!>NH$, by the same method as that by which piperidine had been obtained from pentamethylenediamine, and pyrrolidine was also synthesised by reducing succinimide with sodium and alcohol (*Ber.*, 1887, **20**, 2215). The action of heat on ethylenediamine hydrochloride resulted in the formation of a base (*Ber.*, 1888, **21**, 758; 1890, **23**, 3740; 1891, **24**, 2400), which is now well known as piperazine.

$$NH<\begin{matrix} CH_2\cdot CH_2 \\ CH_2\cdot CH_2 \end{matrix}>NH.$$

By the distillation of ethylenediamine hydrochloride with sodium acetate he obtained a base, lysidine, $\begin{matrix} CH_2\cdot NH \\ | \\ CH_2\text{---}N \end{matrix}\!\!\geqslant C\cdot CH_3$ (*Ber.*, 1894, **27**, 2952), identical with a compound prepared by Hofmann (*Ber.*, 1888, **21**, 2332) in an analogous manner. Lysidine, like piperazine, formed with uric acid a salt which was very readily soluble in water (*Ber.*, 1894, **27**, 2952), and clinical experiments, carried out at Ladenburg's suggestion, showed that a case of acute, and also one of chronic arthritis were both quickly cured by large doses of this base.

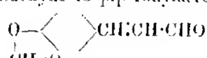
The action of heat on trimethylenediamine hydrochloride resulted, not only in the formation of trimethyleneimine, $CH_2<\begin{matrix} CH_2 \\ CH_2 \end{matrix}>NH$, but also in the production of two picolines (*Ber.*, 1890, **23**, 2727); the production of these two pyridine derivatives was explained by assuming that the diamine first gave rise to a homologue of

piperazine, $NH<\substack{CH_2\cdot CH_2\cdot CH_2\\ CH_2\cdot CH_2\cdot CH_2}>NH$, which then decomposed with formation of ammonia and two molecules of hydrogen, the eight-membered ring suffering disruption, and passing into a mixture of two β-picolines (compare also *Ber.*, 1890, **23**, 2688):



His investigations on pyridine derivatives led him to consider the orientation of the pyridinecarboxylic acids, and he pointed out the important fact that when a pyridinedicarboxylic acid was heated, the α carboxyl group was always the first to be eliminated (*Ber.*, 1885, **18**, 2967). He isolated lutidine (*Ber.*, 1885, **18**, 913) and γ-picoline (*Ber.*, 1888, **21**, 285) from coal tar, and reduced these compounds to the corresponding piperidine derivatives. He showed that α-methyl- and α-ethylpiperidine could be resolved into their optically active components (*Ber.*, 1886, **19**, 2584, 2975), and that picolinic acid (*Ber.*, 1891, **24**, 640), as well as nicotinic and *iso*nicotinic acids (*Ber.*, 1892, **25**, 2768) could be reduced with sodium and alcohol to the corresponding piperidinecarboxylic acids. A summary of his work on pyridine and piperidine derivatives down to 1888 is given in the *Annalen*, 1888, **247**, 1.

The partial synthesis of piperine from piperidine and the chloride of piperic acid having been carried out by Rügheimer in the Kiel laboratory, the last link required to complete the chain was forged by Ladenburg and Scholtz (*Ber.*, 1891, **27**, 2958). Piperonal was condensed with acetaldehyde to piperonylacrolein,



and the latter, with the aid of sodium acetate and acetic anhydride, was converted into an acid,

$$CH_2<\substack{O\\ O}>C_6H_3\cdot CH{:}CH\cdot CH{:}CH\cdot CO_2H,$$

identical with the piperic acid obtained from piperine.

His analytical and synthetical experiments on tropine, which had been interrupted by his work on coniine, were continued intermittently down to 1902. Hydrotropidine hydrochloride, when heated, gave methyl chloride and a base, $C_7H_{13}N$, which he named norhydrotropidine; the hydrochloride of the latter, under similar conditions, gave α-ethylpyridine, together with a small quantity of

a hydrocarbon (*Ber.*, 1887, **20**, 1647). He also showed that tropidine was converted into tropine by treatment with hydrobromic acid (*Ber.*, 1890, **23**, 1780, 2225; 1902, **35**, 1159, 2295).

The resolution of tropic acid into its optically active components (Ladenburg and Hundt, *Ber.*, 1889, **22**, 2590) led to the preparation of optically active atropines, which were obtained by evaporating the active acids with a solution of tropine hydrochloride.

A large proportion of his work on tropine at about this time consisted of repeated but fruitless attempts to synthesise this elusive base. For this purpose, starting from piperidine derivatives, and using Hofmann's method (*Ber.*, 1885, **18**, 111), he prepared various tetrahydropyridine derivatives (*Ber.*, 1887, **20**, 1645) which he thought were related to tropine. He also prepared α-picolylalkine, $C_5NH_4\cdot CH_2\cdot CH_2\cdot OH$, by the condensation of picoline and formaldehyde; this compound on distillation gave vinylpyridine, $C_5NH_4\cdot C_2H_3$, which had a strong odour of conyrine, and on reduction was converted into α-pipecolylalkine,

$$C_5NH_{10}\cdot CH_2\cdot CH_2\cdot OH,$$

a base nearly related to tropine in composition and properties (*Ber.*, 1889, **22**, 2583). These synthetical experiments were, of course, predestined to fail, because they were founded on an erroneous view of the constitution of tropine; this fact, however, does not detract from the value of Ladenburg's positive results, which threw so much light on the nature of tropine and formed so excellent a foundation for the brilliant synthesis ultimately accomplished by Willstätter.

In another long series of papers, published between 1893 and 1906, Ladenburg follows up the discovery of a base which he regarded as a stereoisomeride of coniine. He found (*Ber.*, 1893, **26**, 854) that when coniine hydrochloride was distilled with a relatively small quantity of zinc dust, in addition to conyrine and unchanged coniine, it gave an optically active propylpiperidine, which differed from coniine in specific rotation and in certain other respects. He accounted for the existence of this base, which he named *iso*coniine, by assuming that the arrangement of the atoms or groups around the nitrogen atom was an asymmetric one, or, at any rate, that such an arrangement could modify the optical activity conditioned by the asymmetric carbon group (*Ber.*, 1896, **29**, 2718). By a method similar to that used in the conversion of coniine into *iso*coniine, he prepared from *d*-pipecoline an isomeric base, *iso*pipecoline (*Ber.*, 1894, **27**, 853), and by heating *l*-stilbazoline (*Ber.*, 1903, **36**, 3694), a compound obtained by resolving the reduction product of stilbazole, $C_5NH_4\cdot CH\colon CH\cdot C_6H_5$, he prepared *iso*stilbazoline (*Ber.*, 1904, **37**, 3688). He made many

experiments to try and prove that these optically active *iso*-bases were definite compounds, and not mere mixtures in unequal proportions of the *d*- and *l*-isomerides (*Ber.*, 1895, **28**, 163; 1896, **29**, 2706; 1897, **30**, 485), and he also attempted unsuccessfully to obtain other nitrogenous compounds showing isomerism of the same nature (*Ber.*, 1896, **29**, 2710; 1897, **30**, 1582). In his last paper on this subject (*Ber.*, 1906, **39**, 2486), although he maintained the existence of *iso*coniine, the facts which he himself had established were so difficult to reconcile with his views that he was obliged to conclude that his own synthetical coniine was in reality the *iso*-base, and that the latter was only converted into natural coniine when it was strongly heated. An impartial verdict on this branch of Ladenburg's work may perhaps be implied by the statement that he is not the only chemist who has unsuccessfully devoted time and effort to prove the existence of asymmetry in tervalent nitrogen compounds.

In the course of his experiments on the resolution of piperidine derivatives and during his study of the active bases, Ladenburg made some important contributions to our knowledge of asymmetric compounds. He was the first to show that *dl*-bases could be resolved by the method discovered by Pasteur, and used by the latter for the resolution of *dl*-acids. He also showed that a lowering of temperature occurred when *d*- and *l*-coniine were mixed (*Ber.*, 1895, **28**, 163), whereas no change in temperature was observed in the case of certain other liquids of similar character, having the same specific gravity (*Ber.*, 1895, **28**, 1991). From these facts he argued that *d*- and *l*-coniine united to form a racemic liquid.

A general method for distinguishing solid racemic compounds from *dl*-mixtures was also put forward (*Ber.*, 1894, **27**, 3065), but as the result of adverse criticism, this method was modified as follows (*Ber.*, 1899, **32**, 864): "To decide whether an inactive, resolvable substance is a racemic compound or a mixture of active components, the solubility of the substance is determined with and without the addition of a small quantity of one of the active components (at the same temperature and in the same solvent). If the solubilities are different, the substance is racemic; if the same, it is an enantiomorphous mixture."

During some experiments on the resolution of β-pipecoline with the aid of tartaric acid, he found that when crystallisation occurred at above 100° the experiments failed, whereas at the ordinary temperature the *dl*-base was resolved (*Ber.*, 1894, **27**, 75); also, that the resolution of pyrotartaric acid (methylsuccinic acid) could be accomplished with the aid of strychnine (*Ber.*, 1895, **28**, 1170), but not with quinine. These results led him to conclude that the

dl-base formed with the *d*-acid and the *dl*-acid formed with the *l*-base a salt, one part of the molecule of which was racemic, the other part optically active. To such salts he applied the term half or partly racemic, which had been previously used by E. Fischer (*Ber.*, 1894, **27**, 3225) to denote mixtures, or compounds, of two optically active components which were similar but not enantiomorphously related.

The study of these partly racemic salts was described in numerous papers (*Ber.*, 1898, **31**, 524, 937, 1969; 1899, **32**, 50; 1903, **36**, 1649; 1907, **40**, 2279; 1908, **41**, 966), and a summary of the results was given in the *Annalen* (**364**, 227) in 1909. His experiments were chiefly directed towards obtaining evidence that the two types of partly racemic salts, namely, *d*A*l*B, *l*A*l*B, and *d*A*l*B, *d*A*d*B, were not merely mixtures, but were definite compounds. For this purpose he compared the properties of partly racemic strychnine *dl*-tartrate, *d*A*l*B, *l*A*l*B, with those of the *d*A*l*B and *l*A*l*B salts of strychnine and tartaric acid. He showed that the three compounds differed as regards the hydration of their crystals; also in solubility, specific gravity, specific rotation, and so on; and that the qualitative data could not be reconciled with the view that the partly racemic salt was a mere mixture of the *d*A*l*B and *l*A*l*B components. He also proved that partly racemic strychnine tartrate and brucine hydrogen tartrate had a transition temperature above which they underwent resolution. On the other hand, *dl*-pipecoline *d*-tartrate, which was deposited as a partly racemic salt at high temperatures, had a transition temperature below which it was resolved; *dl*-tetrahydroquinaldine hydrogen *d*-tartrate behaved in a similar manner. From all these results, Ladenburg concluded that the formation of partly racemic salts was a very general phenomenon; further, that the formation of such salts was strong evidence in support of the view that racemic compounds could exist in a dissolved state.

In 1898 he was able to break new ground with the aid of an apparatus for the liquefaction of air. He described various lecture experiments suitable for the illustration of low temperature effects (*Ber.*, 1898, **31**, 1968), and also determined the specific gravities of liquid air and other liquefied gases (*Ber.*, 1899, **32**, 46), as well as their boiling points (*Ber.*, 1899, **32**, 1818). He liquefied ozonised oxygen (*Ber.*, 1898, **31**, 2508), purified the ozone by fractional evaporation, and determined the density of this purified material with the aid of Schilling's apparatus; the purity of the samples, that is to say, the proportion of ozone which they contained, was checked by a titration of the iodine liberated from potassium

iodide by a known quantity of the gas. The density was thus found to be 1·456 (O=1).

In other papers (*Ber.*, 1898, **31**, 2830; 1900, **33**, 2283) dealing with this matter, he replied to objections which had been raised to his method on the grounds that he had used the formula O_3 for ozone in calculating the proportion of this gas in his samples. He then worked out the details of a process for estimating the ozone in a weighed quantity of ozonised oxygen with the aid of turpentine (*Ber.*, 1901, **34**, 631); he was thus able to determine the density of ozone without the use of potassium iodide. Later still (*Ber.*, 1901, **34**, 1184) he showed that the usual method for the estimation of ozone, with the aid of an acidified solution of potassium iodide, gave results which were 50 per cent. higher than the true values, but that correct estimations could be made if the gas were first absorbed in neutral solutions of potassium iodide, which were then acidified before titration.

The interesting question as to the relative positions of iodine and tellurium in the periodic system led Ladenburg to take up the study of the first-named element. He showed (*Ber.*, 1902, **35**, 1256) that silver iodide could be readily freed from silver chloride by repeated extraction with a concentrated solution of ammonium hydroxide until the solubility of the iodide became constant; he reduced the pure iodide with zinc and sulphuric acid, decomposed the zinc iodide which was thus formed with nitrous acid, and distilled the well-washed precipitated iodine in steam. He then determined the melting point, boiling point, and specific gravity of the pure halogen.

Shortly afterwards (*Ber.*, 1902, **35**, 2275) he made a series of determinations of the atomic weight of iodine, based on the conversion of silver iodide into silver chloride and a knowledge of the atomic weights of silver and chlorine. From the results of this work, he found the atomic weight, I=126·96, a value considerably higher than that (126·85) obtained by Stas, but which approximates very closely to that (126·92) which is given in the last report of the International Committee on Atomic Weights.

A list of Ladenburg's papers is given in the *Berichte* (1912, **45**, 3636).

CCIII.—*The Mechanism of the Condensation of Glucose with Acetone.*

By James Leslie Auld Macdonald (Carnegie Scholar).

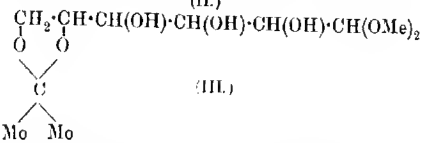
During the past five years the preparation of glucose-monoacetone and -diacetone has been carried out in this laboratory on twenty occasions, the process being modified in various ways (Irvine and Scott, this vol., p. 563). The yields obtained have been very irregular, and, what is more surprising, the amount of monoacetone derivative fluctuated in the most remarkable manner. The conclusion drawn is that the simplest possible explanation, namely, that the reaction consists of the simultaneous hydrolysis of glucosedimethylacetal and condensation with the solvent acetone, is untenable. Such a process should result, in the first instance, in the formation of a glucosidic monoacetone derivative, followed by a second condensation with the ketone, the final product being entirely glucosediacetone. The following research was undertaken in the hope of tracing the mechanism of the reaction, so as to improve the working methods of preparing these derivatives and to throw light on their constitution, as they may play an important part in the future development of synthetical work in the sugar group.

As glucosemonoacetone possesses a glucosidic structure, the formation of the compound must of necessity involve a process of simultaneous hydrolysis and condensation, in which glucosedimethylacetal parts with the acetal grouping and reacts with the solvent ketone. A reaction of this kind does not account for the persistence of glucosemonoacetone however long the treatment with the ketone may be extended. This type of reaction is, moreover, uncommon in the sugar group, and does not take place to any appreciable extent with acyl derivatives of glucose; thus, α-penta-acetyl glucose, when dissolved in acetone containing the same percentage of hydrogen chloride as is necessary for the decomposition of glucosedimethylacetal, readily lost the acyl groups at the temperature of the room, but *no condensation with the solvent took place*, and the main product consisted of glucose. An attempt was therefore made, starting from glucosedimethylacetal, to arrest the condensation at the earliest possible stage, and thus isolate the first product of the reaction. This was carried out as explained in the experimental part, and a product obtained, which, although too unstable to permit of analysis, possessed the reactions which would be char-

[char]acteristic of a glucosedimethylacetalmonoacetone. The first stages of the reaction are therefore expressed in the following scheme:

$C_6H_{12}O_6 \rightarrow$
(I.)

$HO{\cdot}CH_2{\cdot}CH(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CH(OMe)_2 \rightarrow$
(II.)


(III.)

Since glucosedimethylacetalmonoacetone is the main product of the initial stages of the condensation of acetone with glucosedimethylacetal, a knowledge of its properties should furnish valuable evidence for establishing the mechanism of the formation of glucose-monoacetone and -diacetone.

A most significant property of the compound is that on further treatment with acid acetone it yields glucosediacetone, and it is probable that this is the main route by which the latter compound is formed when prepared by the usual method.

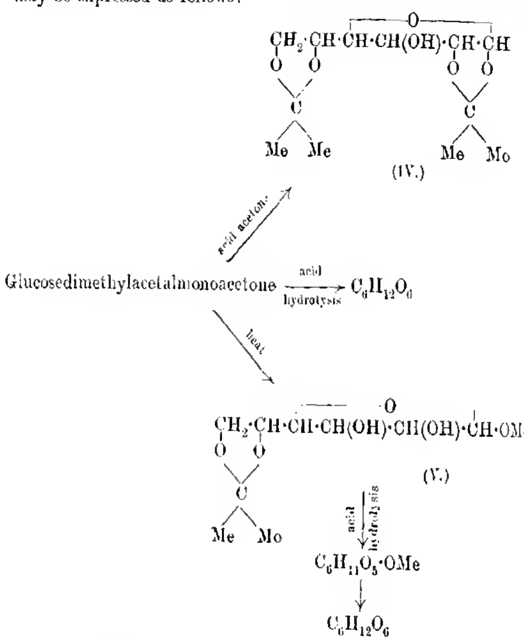
As might be expected, glucosedimethylacetalmonoacetone is extremely unstable, and when heated in a vacuum at as low a temperature as 20° it is readily decomposed, a molecule of methyl alcohol being lost by ring-formation between the α- and δ-carbon atoms, and the γ-oxidic compound,* methylglucosidemonoacetone, is thus produced.

In the light of the above explanation the product of this change should contain a stable glucosidic grouping and an unstable acetone residue. That such is the case was proved by carefully regulated hydrolysis. The crude glucosedimethylacetalmonoacetone was heated in a vacuum until constant in weight, and the syrup obtained hydrolysed with hydrochloric acid of a concentration insufficient to cause decomposition of methyl glucoside. In this way the acetone residue was removed without attacking the glucosidic position, and the final product, as indicated by the rotation value obtained, was an equilibrium mixture of α- and β-methyl glucosides. This result *cannot be explained on any assumption other than the* elimination of methyl alcohol from the acetal and the formation of methylglucosidemonoacetone (V).

* The nomenclature here adopted to express the position of substituent groups in the sugar molecule is the same as that used in this vol., p. 561.

It is perhaps necessary to point out that if the expression "γ-oxidic linking" is to be retained, the adoption of this system involves a certain amount of dubiety, as the γ-linking connects the α- and δ-carbon atoms of the sugar.

Glucosedimethylacetalmonoacetone, like other acetone compounds, is highly sensitive to dilute acids, which remove the acetone residue and simultaneously hydrolyse the acetal grouping, the final product of the reaction being the parent hexose. These reactions may be expressed as follows:



(IV.)

(V.)

Structure and Constitution of Intermediate Compounds.

As Irvine and his collaborators have already pointed out, the position taken up by an acetone residue when entering a sugar molecule, where the number of hydroxyl groups renders the formation of isomeric forms possible, depends largely on the relative stability of the rings thus produced. This stability is influenced by two factors, namely, (*a*) the number of atoms forming the ring, and (*b*) the position of the hydroxyl groups relative to the plane of the γ-oxidic ring of the sugar.

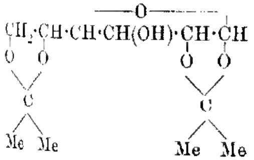
Since glucosedimethylacetalmonoacetone readily forms a glucoside it follows that the acetone residue cannot be linked to the δ carbon atom. Methylglucosidemonoacetone must therefore have two free

hydroxyl groups, and the position of these may be established by methylation and hydrolysis of the resulting compound. This was carried out, and a dimethyl methylglucoside and finally a dimethylglucose were obtained. The general reactions, solubilities, and rotation values of the dimethylglucose thus isolated corresponded with those quoted by Irvine and Scott (this vol., p. 575) for $\beta\gamma$-dimethyl glucose. The optical values are compared below:

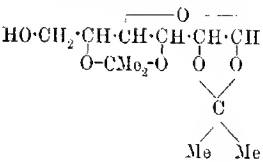
Solvent.	$[\alpha]_D^{20°}$ for dimethylglucose obtained from dimethyl methylglucosidemonoacetone.	$[\alpha]_D^{20°}$ for $\beta\gamma$-dimethylglucose (Irvine and Scott).
Water.............	+65·3°	+64·4°
Methyl alcohol ...	+57·2	+58·1 *
Ethyl alcohol ...	+50·0	+49·4

* New determination.

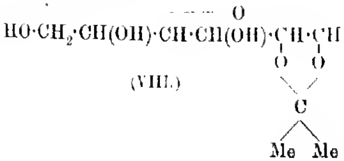
Although the methylated sugar could not on this occasion be obtained crystalline, the resemblance is sufficiently striking to warrant the conclusion that the compound is $\beta\gamma$-dimethylglucose. From this it follows that the acetone residue in methyl glucosidemonoacetone and glucosedimethylacetalmonoacetone is linked to carbon atoms ϵ and ζ. Now, since glucosediacetone is obtained by further condensation of acetone with glucosedimethylacetalmonoacetone, it follows that the acetone residue not attached to the reducing group in this compound is in the $\epsilon\zeta$-position. This is not in agreement with the constitution assigned to glucosediacetone by Irvine and Scott (this vol., p. 564), although it was there pointed out that the evidence on which the suggested constitution is based was capable of a different interpretation. Glucosediacetone formed in the manner now described must have the following structure (VI), provided that the glucosidic acetone residue forms a five-membered ring. Formula (VII) represents the alternative constitution advanced by Irvine and Scott:



(VI.)



(VII.)



(VIII.)

If the above reasoning be accepted the monomethyl glucose described by Irvine and Scott must have the alkyl group in the γ-position, and this conclusion harmonises with all the available evidence regarding the structure of this compound. It may be mentioned here that an extended investigation of the sugar has now been commenced in this laboratory. It is evident, however, that glucosediacetone may also be formed by a different route. When acid acetone is brought into contact with glucosedimethylacetal the first reaction may be the hydrolysis of the acetal grouping and the entry of a molecule of acetone in the $\alpha\beta$-position producing the glucosemonoacetone isolated by Fischer (*Ber.*, 1895, **28**, 2496), formula (VIII), which in turn condenses with a second molecule of acetone to form the di-derivative. The second molecule of acetone may be attached in three alternative ways; the linking may be γ and ζ, γ and ϵ, or ϵ and ζ. The first possibility may be rejected on stereochemical grounds, since a seven-membered ring is involved. Comparing the two remaining alternatives, it will be seen that formula (II) requires the formation of a six-membered ring having a *trans*-configuration in respect of the γ-oxidic ring, a condition involving severe molecular strain. Formula (I) is therefore the more probable, and the fact that only one glucosediacetone has been isolated, although not conclusive, tends to strengthen this view.

The series of probable changes which take place in the formation of acetone derivatives of glucose are thus expressed in the following scheme:

Glucose

↓

glucosedimethylacetal ⟶ methylglucoside

↙ ↘

glucosemonoacetone   glucosedimethylacetalmonoacetone

↘ ↙ ↓

glucosediacetone   methylglucosidemonoacetone.

A review of the whole sequence of changes indicates in a striking manner the complexities introduced into the reactions of the sugars when the latter are converted, even temporarily, into straight-chain derivatives of an acetal nature.

Experimental.

Glucosedimethylacetal.

The conditions laid down by Fischer (*loc. cit.*) were, in essentials, followed in the preparation of this compound. Inasmuch as the preparation was carried out on a much larger scale than that employed by Fischer, it was found convenient, in the first place, to make a solution of dry powdered glucose (90 grams) by boiling the sugar with pure dry methyl alcohol, and, after cooling, to add the requisite amount of hydrogen chloride dissolved in methyl alcohol so as to make the final volume 1600 c.c. and the acid content 1·5 per cent. After remaining at the temperature of the room for sixty hours the acid was removed by shaking first with dry powdered barium carbonate and finally with silver carbonate. After shaking with freshly ignited animal charcoal the solvent alcohol was removed at 35°/15 mm., a Winchester bottle being used as a distilling flask. The syrupy residue was well shaken with 300 c.c. of dry acetone, which was subsequently removed in a vacuum. In this way a clear, colourless syrup was obtained lining the sides and bottom of the bottle, these conditions being extremely well adapted for the subsequent treatment with acetone.

Glucosedimethylacetalmonoacetone.

Five hundred c.c. of dry acetone containing 0·5 per cent. of hydrogen chloride were added to the crude glucosedimethylacetal, and the contents of the bottle were subjected to alternate shaking and heating on the water-bath at 35° for three and a-quarter hours. To aid the incorporation of the syrup with the acetone some chips of porous porcelain were added. The acetone liquor was poured off, and immediately neutralised with barium carbonate, followed by treatment with silver carbonate and charcoal. The undissolved syrup remaining in the bottle was given a further treatment with acid acetone for the same period. A third treatment yielded a negligible amount of product. Extracts 1 and 2 were mixed and dried over anhydrous sodium carbonate. The solution was then concentrated to about one third of the volume over fresh carbonate on the water-bath, filtered, and concentrated further in a vacuum at a low temperature. When the liquor had become slightly syrupy the concentration was stopped, and a large volume of dry light petroleum added. This precipitated a transparent, colourless, mobile syrup, from which the mother liquor was poured away, and fresh quantities of light petroleum were added from time to time. The deposition of the syrupy product extended over several weeks.

The product, which amounted to 25 per cent. of the glucose used was extremely soluble in water, cold acetone, or warm ethyl acetate.

The reactions of the compound were essentially the same as those of glucosedimethylacetal, but the increased solubility indicated that condensation with acetone had proceeded. All attempts to confirm the idea that the syrup consisted of glucosedimethylacetal-monoacetone by means of analyses were fruitless. When dried in a high vacuum at the minimum possible temperature the combustion results obtained corresponded with those required for methyl-glucosidemonoacetone, indicating that a molecule of methyl alcohol had been removed during the drying process.

Hydrolysis of Glucosedimethylacetalmonoacetone.

Hydrolysis of glucosedimethylacetalmonoacetone syrup, which had been heated in a vacuum at 30° until constant in weight, was carried out under conditions which do not affect methylglucoside.

A 2·5 per cent. solution of the syrup was prepared in 50 per cent. ethyl alcohol containing 0·5 per cent. of hydrogen chloride, and the solution examined polarimetrically in a jacketed tube, which was maintained at 30°. Under these conditions hydrolysis was complete in eighty hours. Some of the readings obtained are appended:

Time in hours.	$\alpha^{30°}$.	$[\alpha]_D^{30°}$.
0	−0·74°	−15·10°
1	0·79	−16·12
3	−0·62	−12·65
6	−0·29	−5·29
9	−0·04	−0·82
19	+0·60	+12·24
26	+1·00	+20·40
30	+1·20	+24·49
40	+1·49	+30·40
63	+1·87	+38·16
80	+1·89	+38·57

$l = 2$.

Methylglucoside-εζ-monoacetone.

The crude glucosedimethylacetalmonoacetone described above was dried at 22°/12 mm. until constant in weight. A colourless syrup then remained, which could not be obtained crystalline.

Found: C = 51·19; H = 7·71; OMe = 11·2.

$C_9H_{15}O_5 \cdot OMe$ requires C = 51·25; H = 7·69; OMe = 13·2 per cent.

The following rotation values were observed:

Solvent.	c.	l.	$\alpha^{20°}$.	$[\alpha]_D^{20°}$.
Methyl alcohol	4·451	1	−0·52°	−11·68°
Ethyl alcohol	4·110	1	−0·47	−11·43

The compound, which was practically devoid of action on Fehling's solution, was readily soluble in water, methyl and ethyl alcohol, acetone, ethyl acetate, or ether, but only moderately so in methyl iodide. When heated in a vacuum at 60° for some time it was partly hydrolysed, and gave an insoluble residue when extracted with dry ether. The reactions and solubilities of this residual product agreed with those of methyl glucoside, thus indicating that the acetone residue had been removed.

βγ-Dimethyl Methylglucoside-εζ-monoacetone.

The alkylation of the methylglucosidemonoacetone was carried out by the silver oxide method in the usual way. Three times the theoretical quantity of alkylating mixture was used, and, owing to the sparing solubility of the unalkylated compound in methyl iodide, a few c.c. of acetone had also to be added in the first methylation. To ensure complete alkylation two further treatments were given. On working up the final product in the usual manner a syrup (b. p. 142—143°/12 mm.) was obtained, having no action on Fehling's solution. The yield was slightly less than the weight of unalkylated material used.

Found: C = 54·53; H = 8·45; OMe = 32·2.

$C_9H_{13}O_3(OMe)_3$ requires C = 54·96; H = 8·40; OMe = 35·5 per cent.

Solvent.	*c*.	*l*.	$\alpha^{20°}$.	$[\alpha]_D^{20°}$.
Methyl alcohol	6·11	1	− 1·16°	− 19·00°
80 per cent. ethyl alcohol	10·0	2	− 2·98	− 15·00

βγ-Dimethyl Methylglucoside.

A 10 per cent. solution of dimethyl methylglucosidemonoacetone in 80 per cent. alcohol containing 0·5 per cent. of hydrogen chloride was heated in boiling water for twelve hours, during which time the rotation altered from lævo to dextro and became constant. After neutralisation with silver carbonate the solvent was removed in a vacuum, and the resulting syrup dissolved in dry acetone. This solution was dried over magnesium sulphate, the solvent evaporated, and the residue extracted repeatedly with dry ether. After removal of the solvent in a vacuum an attempt was made to distil the product; a fraction almost without action on Fehling's solution and showing $[\alpha]_D^{20} + 15·28°$ in methyl alcohol was thus obtained. Fractions of higher boiling point were more strongly dextro-rotatory, the maximum optical value recorded being + 51·1°.

Found: C = 48·05; H = 7·87; OMe = 40·3.

$C_6H_9O_3(OMe)_3$ requires C = 48·65; H = 8·11; OMe = 41·9 per cent.

βγ-Dimethyl Glucose.

Complete hydrolysis of the glucoside described above was readily effected by heating an 8 per cent. solution of the compound in 80 per cent. alcohol containing 8 per cent. of hydrogen chloride at 90° for forty-five minutes. After neutralisation and removal of the solvent in a vacuum a syrup remained, which failed to crystallise, although attempts to affect this were continued throughout several months. (Found, C=45·99; H=7·59; OMe=30·2. $C_6H_{10}O_4(OMe)_2$ requires C=46·15; H=7·69; OMe=29·8 per cent.)

Solvent.	c.	l.	$a^{20°}$.	$[a]_D^{20°}$.
Water.............	1·056	2	+1·38°	+65·3°
Methyl alcohol ...	1·26	1	0·72	57·2
Ethyl alcohol ...	1·617	2	1·67	50·0

I take this opportunity of expressing my thanks to Professor J. C. Irvine for his valuable help and advice, which was at all times at my disposal during the course of this work, and also to the Carnegie Trust for a grant which partly defrayed the expenses of the research.

CHEMICAL RESEARCH LABORATORY,
UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD,
UNIVERSITY OF ST. ANDREWS.

CCIV.—*The Solubilities of Alkali Haloids in Methyl, Ethyl, Propyl, and* iso*Amyl Alcohols.*

By WILLIAM ERNEST STEPHEN TURNER and CRELLYN COLGRAVE BISSETT.

THE particular salts included in the scope of this investigation are lithium chloride and iodide, sodium chloride and iodide, potassium chloride, bromide and iodide, and rubidium chloride, of which we required information as to their solubility in connexion with other physical measurements in progress. The solubilities in water of all the salts mentioned had previously been measured, thus making possible a comparison with the solvent action of the alcohols, and a few measurements in the alcohols, to be referred to later, had also been carried out by various investigators.

The work detailed in this paper falls into three sections, namely, (1) the determination of the compounds formed between the alcohol and the salt at the temperature of the solubility measurements,

(2) the construction of the solubility curve of lithium chloride in ethyl alcohol for the temperature range 0—60°; and (3) the comparison of the solubilities of the salts at a common temperature of 25°.

The salts, initially the best commercially obtainable, were subjected to purification until analysis proved them to be pure. Rubidium chloride was prepared from a mixture of the bromide and iodide by the action of moist silver oxide and subsequent neutralisation of the base.

Some initial difficulty was experienced in obtaining the lithium salts, especially the iodide, quite free from water, but this was overcome finally by electrical heating in a vacuum, using the apparatus already described by us (P., 1913, **29**, 233).

The alcohols were thoroughly desiccated, the methyl and ethyl by lime, the propyl and *iso*amyl alcohols by anhydrous copper sulphate, and subsequently fractionated, most of the fractions being collected over a range of less than 0·1°.

Compounds of the Alkali Haloids with Alcohols.

As soon as the solubility measurements had been completed, the composition of the solid phase was determined in each case in the following manner. The solid was rapidly collected, removed to a porous porcelain tile, and placed in a desiccator containing a quantity of the pure solvent. This desiccator was in turn placed in the thermostat at the same temperature as that at which the solubility was determined, and the salt allowed to dry under these conditions. When ready for analysis the halogen content of a weighed portion was determined by the use of standard silver and potassium thiocyanate solutions.

Lithium Chloride and Methyl Alcohol.—Simon (*J. pr. Chem.*, 1879, [ii], **20**, 371) described a compound of the composition $LiCl,3CH_4O$, obtained by cooling a saturated solution of the salt to a temperature of $-16°$ to $-18°$. This compound he speaks of as melting when its temperature is raised to that maintained in the laboratory. We found that the solid phase at 25° consists of the anhydrous salt.

Lithium Chloride and Ethyl Alcohol.—At 25° the solid phase was in this case also found to consist of the anhydrous salt. Simon obtained transparent, prismatic crystals of the composition $LiCl,4C_2H_6O$ by cooling a solution in a freezing mixture. Such a degree of cooling is unnecessary, for we found that the solution saturated at 25° gave a crystalline deposit at the laboratory temperature of about 11—15°. Determinations were accordingly made at a series of temperatures between 0° and 17·1°. The

percentages of lithium chloride found in the compound were, at 0°, 18·73; at 17·1°, 18·48; the calculated value for $LiCl,4C_2H_6O$ is 18·71. The transition point:

$$LiCl,4C_2H_6O \rightleftarrows LiCl$$

was found to lie at 17·4° (see below).

Lithium Iodide and Propyl Alcohol.—The solid phase at 25° crystallised in flat plates of a very deliquescent character, and analysis proved it to contain 35·52 per cent. of lithium iodide. For $LiI,4C_3H_8O$, which is obviously the composition of the compound, the calculated amount of lithium iodide is 35·78 per cent.

Sodium Iodide and Methyl Alcohol.—At 25° the solid phase was composed of the anhydrous salt, but when cooled to a temperature of 15—16° the liquid became packed with a mass of needle-shaped crystals, which were found to contain 61·96 per cent. of sodium iodide, whilst the calculated percentage for $NaI,3CH_4O$ is 60·95. The crystals rapidly effloresce when exposed to air, this fact readily accounting for the somewhat high analytical result.

No other compounds were discovered under the working conditions, although considerable heat was disengaged by the lithium salts and sodium iodide on solution in the various alcohols.

*The Solubility Curve of Lithium Chloride in Ethyl Alcohol.**

A series of measurements of the solubility of lithium chloride in ethyl alcohol was made in the following manner. A Beckmann freezing-point tube was fitted with an air-tight mercury cup-stirrer, of the type described by Findlay ("Practical Physical Chemistry," p. 238), the stem of the stirrer being hollow to permit of the removal of solution by means of a pipette of diameter slightly smaller than the stirrer, whilst the side-tube of the freezing-point tube was connected with U-tubes containing calcium chloride. Excess of solid with the alcohol were placed in the tube, usually

* After the preparation of this paper for publication we found that Lemoine (*Compt. rend.*, 1897, **125**, 603) had made three determinations of the solubility of lithium chloride in methyl alcohol and six in ethyl alcohol. None of his results agrees with ours, and on the face of them, the measurements in ethyl alcohol challenge adverse criticism. Lemoine quotes Simon as proving the existence of the compounds $2LiCl,3CH_4O$ and $LiCl,2C_2H_6O$, whereas Simon himself gives them as $LiCl,3CH_4O$ and $LiCl,4C_2H_6O$, and our work confirms the existence of the latter substance. Lemoine states that his own analysis confirms the composition as $LiCl,2C_2H_6O$. No indication of the solubility method is given, and no determination of the solid phase in contact with the solution made, nor is the temperature given at which the presumed $LiCl,2C_2H_6O$ exists. The values given by Lemoine for solutions in ethyl alcohol are: at 1·6°, 16·28; 5·7°, 16·23; 13°, 14·91; 25°, 15·28; 40·6°, 17·65; 62·6°, 21·96 grams of salt per 100 grams of solvent. It is not easy to construct a curve based on these numbers.

in the form of a mixture of the nearly saturated solution with the excess of the solid phase stable at the temperature of measurement, the mixture being prepared in a tightly-stoppered bottle. The temperature variation of the thermostat used did not exceed 0·05°, except at 60°, where it reached 0·2°, but at this temperature the rate of change of solubility is very small. After vigorous stirring of the mixture for three or four hours, samples of the solution, usually between 1 and 2 grams in weight, were withdrawn by a pipette provided with a tightly packed plug of cotton-wool and an indiarubber clip, which prevented the entrance of air between the pipette stem and the stirrer, and ensured the presence of dry air within the apparatus throughout the determination. The composition of the solution was determined by volumetric analysis, as already described. Further samples were withdrawn at intervals of an hour until saturation was reached. As a rule, the first sample removed was found, on comparison with the later results, to be already saturated.

At each temperature the composition of the solid phase was determined in the manner given in the first section.

The results of the determinations are embodied in the following table:

Temperature.	Solid phase.	Grams of anhydrous lithium chloride dissolved by 100 grams of ethyl alcohol.
0°	$LiCl,4C_2H_6O$	14·42
5	$LiCl,4C_2H_6O$	15·04
10	$LiCl,4C_2H_6O$	16·77
15	$LiCl,4C_2H_6O$	18·79
17	$LiCl,4C_2H_6O$	20·31
20	LiCl	24·28
30	LiCl	25·10
40	LiCl	25·38
50	LiCl	24·40
60	LiCl	23·46

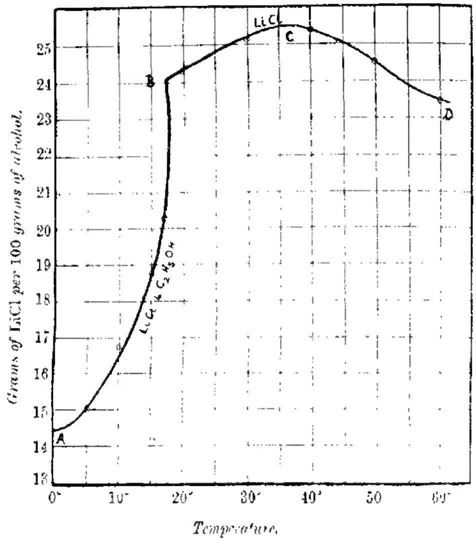
From the numbers given it will be seen that the rate of increase of solubility is most rapid between the temperatures 15° and 20°, and the determination at 17° was afterwards made both to confirm this rapid rise and to fix the position of the first portion of the solubility curve, which is produced below.

The full curve *ABCD* consists of two separate portions intersecting at *B*, the point which indicates the transition point of the alcoholate. Read from the curve, the change point is 17·4°, and this temperature received confirmation by experiments on the growth or disappearance of the crystalline phase, $LiCl,4C_2H_6O$. For this purpose the behaviour of a mixture of the solution, and the crystalline and anhydrous solid phases contained in a tightly-closed vessel was closely watched as the temperature was very slowly

altered over the range 17—18°. The deposition of the crystalline form was found clearly to occur up to a temperature of 17·1°, whilst at 17·6° the anhydrous slowly grew at the expense of the crystalline variety. Confirmation was made of these visual tests by analysis, and it was proved that at 17·6° the anhydrous salt formed the solid phase, whilst at 17·1° it consisted of the alcoholate. The transition point accordingly lies at about 17·4°.

The Comparative Solubilities at 25°.

The method adopted in measuring the solubilities at 25° was very similar to that in a former investigation (Peddle and Turner,



this vol., p. 1202), excess of the very finely powdered and thoroughly dried salts being agitated in small, perfectly ground, stoppered bottles with the alcohol used as solvent. Initially the mixture was maintained for some time at 40°, then transferred to the thermostat at 25°, and thoroughly agitated from time to time. Samples for analysis were first withdrawn after forty-eight hours and then afterwards at twenty-four-hour intervals, the total period of the test extending usually to nine or ten days. The amounts of solution removed for analysis varied from 0·5 to 5 grams for

the more soluble substances, and as much as 20 or 60 grams with the salts only sparingly soluble in propyl or *iso*amyl alcohols. Before the aqueous solution of the sample was prepared for analysis, the alcohol was removed by evaporation, save, as happened with the iodide solutions, when decomposition of the salt began as a result of the evaporation. Despite the use of brown-coloured bottles, the iodide solutions after some days developed a brown tint due to traces of iodine.

In one instance, namely, the solubility of lithium iodide in amyl alcohol, the method employed was that used in determining the solubility curve of lithium chloride in ethyl alcohol, for the viscosity of the solution prevented rapid diffusion through the liquid, and necessitated continuous stirring.

The collected results are given in the following table, the figures representing the number of grams of the anhydrous salt dissolved by 100 grams of the solvent. In order to compare the solvent action of the alcohols with that of water, determinations in the last-named solvent are included in the table. In four cases the solid phases actually present are not the anhydrous forms, but, in water, $LiCl,H_2O$, $LiI,3H_2O$, and $NaI,3H_2O$; in propyl alcohol, $LiI,4C_3H_8O$.

	Solvent.				
Substance.	H_2O.	CH_4O.	C_2H_6O.	C_3H_8O.	$C_5H_{12}O$.
LiCl	83·37[1]	42·36	25·83	16·22	9·03
LiI.........	168·5[2]	343·4	250·8	47·52	112·5
NaCl	36·05[3]	1·31	0·065	0·012	0·002
NaI	184·5[4]	90·35	46·02	28·22	16·30
KCl	39·90[5]	0·53	0·022	0·004	0·0008
KBr	67·75[6]	2·17	0·142	0·035	0·005
KI	148·3[7]	18·04	2·16	0·43	0·098
RbCl	94·35[8]	1·41	0·078	0·015	0·0025

[1] Kremers, *Ann. Phys. Chem.*, 1856, [ii], **99**, 47.
[2] *Ibid.*, 1858, [ii], **103**, 65.
[3], [5] and [8] Berkeley, *Phil. Trans.*, 1904, **203**, *A*, 208.
[4] and [6] De Coppet, *Ann. Chim. Phys.*, 1883, [v], **30**, 425.
[7] Landolt-Börnstein "Tabellen," 1905.

Patten and Mott (*J. Physical Chem.*, 1904, **8**, 157) made determinations, without describing the method, of the solubility of lithium chloride in a series of alcohols, but their results in two out of the three comparable cases are totally different from ours. Their figures for the percentage of the salt in the solution are, in ethyl alcohol, 2·475; in propyl alcohol, 3·720; in butyl alcohol, 9·56; in *iso*amyl alcohol, 8·26. There is close agreement between their value for amyl alcohol and ours, which when calculated to the percentage basis is 8·29, but unaccountable divergence in the other instances. All our measurements go to prove that the haloid salts

are decreasingly soluble as one passes from water along the series of alcohols. There is no regularity in Patten and Mott's figures.

A few other measurements are available for comparison; de Bruyn (*Zeitsch. physikal. Chem.*, 1892, **10**, 782) deduced from experiment the following solubilities, in grams dissolved by 100 grams of the solvent: sodium chloride, 1·41 in methyl and 0·065 in ethyl alcohol at 18·5°; sodium iodide, 77·7 and 43·1 respectively at 22·5°; potassium chloride, 0·5 and 0·034 at 18·5°; potassium bromide, 1·51 and 0·13 at 25°; potassium iodide, 16·5 and 1·75 at 20·5°. The values for sodium iodide and potassium bromide in methyl alcohol are both low, but in the other cases, allowing for temperature differences, there is fair agreement between our and de Bruyn's numbers.

For potassium iodide, Walden (*Zeitsch. physikal. Chem.*, 1906, **55**, 683) found values at 25°, in methyl alcohol 14·97, in ethyl 1·92, and our numbers, when reduced to the same basis, are in good agreement.

Turning now to a consideration of our data, three very clear regularities manifest themselves. First, with the single exception of lithium iodide, the solubility decreases as we pass from water and ascend the series of alcohols; and it must be remembered that the two numbers for lithium iodide which break the regularity of the series, namely, those in water and in propyl alcohol, are the solubilities for the hydrate and alcoholate respectively, whereas for the same substance and the other three alcohols the numbers represent the solubilities of the uncombined salt.

Next, solubility in water and the alcohols increases in the order chloride, bromide, iodide. There is no exception to this rule.

Finally, rubidium chloride shows an interesting divergence from the regular order in the series of the alkali chlorides, the order of solubilities being lithium chloride>sodium chloride>rubidium chloride>potassium chloride. This is true of all five solvents.

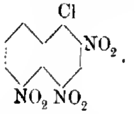
We desire to express our thanks to the Government Grant Committee of the Royal Society for a grant which assisted us to purchase solvents used in this investigation.

Chemistry Department,
The University, Sheffield.

CCV.—*Nitration of* 1-*Chloro*-2 : 4-*dinitronaphthalene.*

By Max Rindl.

The readiness with which 1-chloro-2 : 4-dinitronaphthalene can be prepared from Martius yellow by the action of *p*-toluenesulphonyl chloride and diethylaniline (Ullmann and Bruck, *Ber.*, 1908, **41**, 3932) has suggested the use of this material as the starting point in the preparation of trinitronaphthalene derivatives. By the nitration of chlorodinitronaphthalene a mixture of two isomeric chlorotrinitronaphthalenes is obtained. The relative quantities of these two products are such that one may be regarded as a by-product. The principal isomeride has the constitution:



Its chlorine atom is replaceable by the hydroxyl group, and the trinitronaphthol so formed yields on oxidation with nitric acid 3-nitrophthalic acid. The third nitro-group must therefore have assumed one of the α-positions in the unsubstituted benzene nucleus. The trinitronaphthol derived from the above chlorotrinitronaphthalene proves to be identical with the trinitronaphthol resulting from the treatment of 5-nitro-4-nitroso-α-naphthol with dilute nitric acid, and which has been proved to be 2 : 4 : 5-trinitro-α-naphthol (Graebe, *Ber.*, 1899, **32**, 2878).

The second product formed in the nitration process must be 1-chloro-2 : 4 : 8-trinitronaphthalene, since the trinitronaphthol derived from it is identical with the trinitronaphthol obtained by treating 8-nitro-4-nitroso-α-naphthol with dilute nitric acid (Graebe, *Ber.*, 1899, **32**, 2879).

Under the acidifying influence of the three nitro-groups the chlorine atom is extremely mobile. In this respect 1-chloro-2 : 4 : 5-trinitronaphthalene presents an analogy to picryl chloride; thus on boiling with a dilute aqueous solution of alkali hydroxide it is converted into trinitronaphthol. The replacement of the chlorine atom by the hydroxyl group can even be effected by sodium carbonate. The trinitronaphthol so obtained is a dye, but the expectation that the newly-introduced nitro-group would function as an auxochrome was not realised. The shade of colour is the same as that produced by Martius yellow, the intensity, however, being markedly diminished.

Other groups can be substituted for chlorine in 1-chloro-2 : 4 : 5-

trinitronaphthalene with the greatest facility, such as the methoxyl, amino-, and anilino-groups.

Experiments undertaken with a view to prepare dinaphthyl derivatives by removing the chlorine atom with finely-divided copper, and thus joining two naphthalene molecules, although not entirely successful, nevertheless demonstrated the possibility of thus obtaining dinaphthyl compounds. From 1-chloro-2:4:5-trinitronaphthalene, hexanitrodinaphthyl should have been formed. The investigation of the main product of the reaction was abandoned after repeated futile attempts at purification. An interesting secondary reaction, however, took place, resulting in the substitution of chlorine by hydrogen with the formation of 1:3:8-trinitronaphthalene, thus supplying additional evidence in favour of the constitution given above. In the case of 1-chloro-2:4-dinitronaphthalene, tetranitrodinaphthyl was easily obtained.

An interesting observation, which seems to indicate a case of steric hindrance, was made when attempting to reconvert the two trinitronaphthols into the chlorotrinitronaphthalenes from which they were originally prepared. Whilst *p*-toluenesulphonyl chloride and diethylaniline readily act on 2:4:5-trinitro-α-naphthol, not a trace of 1-chloro-2:4:8-trinitronaphthalene could be obtained from 2:4:8-trinitro-α-naphthol by similar treatment.

Experimental.

Nitration of 1-Chloro-2:4-dinitronaphthalene.

The chlorodinitronaphthalene prepared from 2:4-dinitro-α-naphthol was added in small portions to concentrated nitric acid (D 1·52), the acid being cooled by immersion in cold water. As the result of a large number of experiments, it was found that the maximum yield was obtained if the quantity of chlorodinitronaphthalene compared to that of nitric acid was as 1 to 2·5 or 3. After several days, transparent, hexagonal prisms of chlorotrinitronaphthalene began to separate out, which were collected from time to time and dried on porous plates. The first fraction, which was quite uniform, was subsequently shown to be *1-chloro-2:4:5-trinitronaphthalene*. After a period, which varied slightly with the conditions of experiment—being on an average twenty-one days—amorphous, granular aggregates began to separate out, together with the prisms in gradually increasing quantities, the quantity of the prismatic substance meanwhile decreasing. The crops of prisms were recrystallised from glacial acetic acid, forming tiny, white needles with a tinge of yellow, and melting at 113—114°.

The substance is insoluble in light petroleum, sparingly soluble in alcohol, and readily so in benzene or acetic acid.

Found: C=40·40; H=1·70; N=14·22.

$C_{10}H_4O_6N_3Cl$ requires C=40·32; H=1·36; N=14·15 per cent.

Separation of the Isomeric Chlorotrinitronaphthalene.

A partial separation of the two isomeric chlorotrinitronaphthalenes which crystallise out together as the nitration process continues can be effected by fractional crystallisation from glacial acetic acid. The more sparingly soluble compound, melting at 143–144°, separates out first. By recrystallising the later fractions several times from the same solvent the second isomeride was obtained, although apparently not in a pure state. It melts between 118° and 126°.

Found: N=14·22; Cl=11·61.

$C_{10}H_4O_6N_3Cl$ requires N=14·15; Cl=11·91 per cent.

Conversion of 1-Chloro-2:4:5-trinitronaphthalene into 2:4:5-Trinitro-α-naphthol.

Three grams of finely divided 1-chloro-2:4:5-trinitronaphthalene (1 molecule) were suspended in a little water or alcohol, and boiled for half-an-hour after the addition of the theoretical quantity (20 c.c., corresponding with 2 molecules) of *N*/10-sodium hydroxide solution. Sodium hydroxide is preferable to potassium hydroxide on account of the greater solubility of the sodium salt of trinitronaphthol. As the conversion took place, the naphthol salt dissolved to a reddish-brown solution. After completion of the reaction the solution was concentrated, and decomposed with dilute hydrochloric acid. The yellow, flocculent precipitate was collected, washed with as little water as possible, and dried. When crystallised from acetic acid it formed yellow leaflets melting at 186° (corr. 190°). (Found, C=42·87; H=2·12; N=15·24. $C_{10}H_5O_7N_3$ requires C=42·98; H=1·81; N=15·09 per cent.)

On evaporating to dryness a suspension of the above compound in very dilute nitric acid, a residue of 3-nitrophthalic acid remained. This trinitronaphthol agrees in all its properties with the 2:4:5-trinitro-α-naphthol obtained by acting on 5-nitro-4-nitroso-α-naphthol with warm dilute nitric acid (Graebe, *Ber.*, 1899, 32, 2877), a mixture of the two showing no depression of the melting point.

Formation of 1:3:8-*Trinitronaphthalene.*

A solution of 1-chloro-2:4:5-trinitronaphthalene was treated with copper powder, with the object of obtaining hexanitrodinaphthyl, as follows:

Ten grams of the substance were dissolved in 40 grams of nitrobenzene and the solution was heated, after the addition of 10 grams of copper powder, for fifteen minutes under reflux. The hot solution was filtered, and the filtrate distilled in a current of steam in order to remove the nitrobenzene. The greyish-black solid residue was extractel for two days in a Soxhlet apparatus with benzene. The resinous, brown extract was concentrated and crystallised several times from glacial acetic acid with addition of animal charcoal. Finally, a solid was obtained melting at 212—213° (corr. 218—219°), which proved to be identical with 1:3:8-trinitronaphthalene (Beilstein and Kuhlberg, *Annalen*, 1873, **169**, 96; Friedländer, *Ber.*, 1899, **32**, 3531). (Found, N=16·17. $C_{10}H_5O_6N_3$ requires N=16·01 per cent.)

The dark residue remaining in the Soxhlet apparatus after extraction of the 1:3:8-trinitronaphthalene with benzene is insoluble in most solvents. It dissolves in hot concentrated nitric acid, but is reprecipitated in the same impure state. A solution in pyridine remained black and opaque even after boiling for hours with animal charcoal, and showed no tendency to crystallise on concentration. Addition of alcohol, acetic acid, and acetone produced only resinous, black precipitates. As a last resort, the solution was left for weeks over zinc chloride in a vacuum desiccator, but as no better results were realised the examination of this substance was discontinued.

Conversion of 2:4:5-*Trinitro-α-naphthol into* 1-*Chloro*-2:4:5-*trinitronaphthalene.*

The displacement of the hydroxyl group by chlorine can be effected by means of *p*-toluenesulphonyl chloride and diethylaniline in much the same way as has been done in the case of 2:4-dinitro-α-naphthol. A slight modification of the method adopted with the latter substance, however, is necessary.

2·8 Grams of 2:4:5-trinitro-α-naphthol (1 molecule) were thoroughly mixed with 2·85 grams of *p*-toluenesulphonyl chloride (1½ molecules), 6·4 c.c. of diethylaniline (4 molecules) were added, and the mixture was heated for an hour on the steam-bath with frequent stirring. After cooling, the unchanged diethylaniline was removed as the hydrochloride, by adding dilute hydrochloric acid, stirring, and decanting. A pasty mass remained, from which

unchanged *p*-toluenesulphonyl chloride was removed by boiling with a little alcohol. 1-Chloro-2:4:5-trinitronaphthalene remained as a brown powder, which was purified by washing with water, drying, treating with very dilute aqueous ammonia, and finally crystallising from glacial acetic acid. The product melted at 143–144°. (Found, N=13·95. Calc., N=14·15 per cent.)

2:4:5-*Trinitro-α-naphthylamine.*

In order to effect the replacement of chlorine by the amino-group, 1·5 grams of 1-chloro-2:4:5-trinitronaphthalene were dissolved in 50 c.c. of amyl alcohol, and gaseous ammonia was passed through the boiling solution. After a short time a yellow precipitate, consisting of a mixture of ammonium chloride and trinitronaphthylamine, began to fall. In order to complete the reaction it was necessary to continue passing the gas through for at least two hours. The alcohol was removed by distillation in a current of steam, and the precipitate collected and washed, until the filtrate ceased to show the chlorine reaction. When crystallised from acetone or glacial acetic acid with addition of animal charcoal the product formed microscopic, yellow prisms, melting at 305°, having previously changed colour to brown and black. An aqueous solution of alkali hydroxide converts the trinitronaphthylamine into the alkali salt of trinitronaphthol, which dissolves with a red colour. 2:4:5-*Trinitro-α-naphthylamine* is insoluble in alcohol, toluene, or light petroleum, sparingly soluble in amyl alcohol or glacial acetic acid, and more readily so in acetone.

Found: C=43·23; H=2·47; N=19·94.

$C_{10}H_6O_6N_4$ requires C=43·13; H=2·18; N=20·19 per cent.

2:4:5-*Trinitro-α-phenylnaphthylamine.*

Aromatic amines condense with 1-chloro-2:4:5-trinitronaphthalene to form trinitroarylnaphthylamines. One molecular proportion of chlorotrinitronaphthalene was dissolved in a little benzene, and two molecular proportions of aniline were added. The colour changed to red, a violent reaction set in, and the whole mass solidified. In order to remove the aniline hydrochloride formed in the reaction the product was boiled with water. The red, crystalline residue was collected, dried, and recrystallised from glacial acetic acid, from which it separated in plates melting at 218·5°. It is insoluble in ether, alcohol, or light petroleum, but moderately soluble in benzene or glacial acetic acid.

Found: C=54·39; H=3·12; N=15·96.

$C_{16}H_{10}O_6N_4$ requires C=54·20; H=2·85; N=15·85 per cent.

2:4:5-*Trinitro-α-naphthylethylamine.*

One gram of 1-chloro-2:4:5-trinitronaphthalene (1 molecule) was dissolved in a little alcohol, and 1·35 grams (3 molecules) of a 33 per cent. alcoholic solution of ethylamine were added. The colour changed to red, and a precipitation of yellow, interlaced needles began. The mixture was kept boiling for about fifteen minutes, filtered, and the precipitate crystallised from benzene or alcohol. The substance melts at 157—159°. It is only very sparingly soluble in ether, but readily so in glacial acetic acid, and is hydrolysed on heating with concentrated solutions of alkali hydroxides.

Found: C = 47·18; H = 3·42; N = 18·46.

$C_{12}H_{10}O_6N_4$ requires C = 47·02; H = 3·30; N = 18·34 per cent.

2:4:5-*Trinitro-α-naphthyldimethylamine.*

The condensation with dimethylamine was effected in the same way as described above for ethylamine. The product crystallised from glacial acetic acid in minute, orange leaflets, melting at 194·5—195·5°.

Found: N = 18·40.

$C_{12}H_{10}O_6N_4$ requires N = 18·34 per cent.

2:4:5-*Trinitro-α-naphthyl Methyl Ether.*

Two grams of 1-chloro-2:4:5-trinitronaphthalene were dissolved in 75 c.c. of methyl alcohol, and to the boiling solution the theoretical quantity (0·36 gram) of sodium methoxide, dissolved in 25 c.c. of methyl alcohol, was added drop by drop. The red solution was boiled for fifteen minutes and cooled, when yellow crystals separated. On recrystallisation from acetic acid these melted at 150·5—151·5°.

Found: C = 44·85; H = 2·71; N = 14·16.

$C_{11}H_7O_7N_3$ requires C = 45·02; H = 2·41; N = 14·37 per cent.

1:3:5-*Trinitronaphthol from 1-Chloro-2:4:8-trinitronaphthalene.*

In order to determine the constitution of the isomeric chlorotrinitronaphthalene, formed as a by-product in the process of nitration, this substance was converted into trinitronaphthol by treatment with an aqueous solution of sodium hydroxide. The method adopted was exactly the same as in the case of 1-chloro-2:4:5-trinitronaphthalene. The product of the reaction was impure, and had to be recrystallised several times from glacial acetic acid before a homogeneous trinitronaphthol was obtained, indicating that the chlorotrinitronaphthalene was not uniform, in spite of the repeated frac-

tional crystallisation. The trinitronaphthol ultimately obtained proved to be identical with that derived from 8-nitro-4-nitroso-α-naphthol. The by-product of the nitration is therefore 1-chloro-2:4:8-trinitronaphthalene.

It seemed interesting to obtain a criterion of the degree of purity of the 1-chloro-2:4:8-trinitronaphthalene by comparing it with the pure product obtained from pure 2:4:8-trinitro-α-naphthol by treatment with *p*-toluenesulphonyl chloride and diethylaniline. The method applied was identical with that adopted in the case of 2:4:5-trinitro-α-naphthol, except that a series of experiments was carried out with varying quantities of the reacting substances. In all cases the unaltered trinitronaphthol was recovered, not a trace having undergone conversion. It is suggested that this might be a case of steric hindrance, due to the nitro-groups in the ortho- and peri-positions.

2:4:2′:4′-*Tetranitro-αα-dinaphthyl.*

In view of the failure to obtain hexanitrodinaphthyl, an attempt was made to couple two chlorodinitronaphthalene molecules together, by heating a solution with copper powder.

Five grams of 1-chloro-2:4-dinitronaphthalene were dissolved in 10 c.c. of nitrobenzene, heated, after the addition of 5 grams of copper powder, for thirty minutes under reflux. After filtration, the filtrate was distilled in a current of steam, and the dark grey residue extracted with ether for several days. From the ethereal extract 2·4 grams of 1:3-dinitronaphthalene were obtained. The residue remaining in the Soxhlet apparatus was dissolved in a considerable quantity of benzene, and, after concentration, was allowed slowly to evaporate. Dark greyish-brown scales separated, which were collected from time to time, dissolved in pyridine, and boiled for an hour with animal charcoal. After concentrating the filtered solution, alcohol was added, when yellow, interlaced needles were precipitated. 2:4:2′:4′-*Tetranitro-αα-dinaphthyl* remained unchanged when heated to 350°. It is sparingly soluble in benzene or acetic acid, more readily so in nitrobenzene or pyridine.

Found: C = 55·52; H = 2·52; N = 13·16.

$C_{20}H_{10}O_8N_4$ requires C = 55·27; H = 2·33; N = 12·93 per cent.

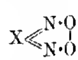
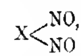
The author desires to thank Professor Ullmann, of the Königliche Technische Hochschule, Charlottenburg, for kind encouragement and advice during the course of this work.

Grey University College.
Bloemfontein, South Africa.

CCVI.—*Constitution of Furoxans (Dioxime "Peroxides").*

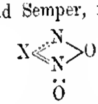
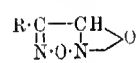
By Martin Onslow Forster and Matthew Felix Barker.

In a communication dealing with the nature of the compounds which arise by heating the *o*-nitrotriazo-derivatives of benzene and naphthalene (Forster and Fierz, T., 1907, **91**, 1942), it was suggested that the numerous aromatic substances previously regarded as dinitroso-compounds should be classified as dioxime peroxides:

 instead of 

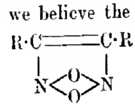
and this proposal remained unchallenged until Green and Rowe (T., 1912, **101**, 2452) claimed for these materials the constitution of furoxans (oxides of furazan), similar in constitution to the aliphatic derivatives described by Wieland and Semper (*Annalen*, 1907, **358**, 36).

During the discussion which followed their paper, however, it was pointed out by one of us that the particular oxide of furazan adopted by Green and Rowe, like the one previously advocated by Wieland and Semper, namely:

 and 

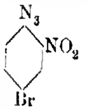
respectively, conflicts with the observation of Forster and Fierz (*loc. cit.*) that when 1-nitro-2-naphthylazoimide and 2-nitro-1-naphthylazoimide are heated, elimination of nitrogen leads to the same dioxime "peroxide" in each case, an origin which points unmistakably to a symmetrical constitution for the furazan oxide.

A reasonable objection to this argument, however, follows from the fact that the transference of oxygen from one atom of nitrogen to the other, demanded in the case of the nitronaphthylazoimides if the formula of Green and Rowe is correct, might be due to the steric effect of the second benzene ring, and we have therefore made experiments to ascertain whether the change in question is independent of the naphthalene nucleus. We find that it is, and are therefore led to the conclusion that these furazan oxides are symmetrical in structure. As stated in a preliminary communication (P., 1913, **29**, 152), we believe the formula:



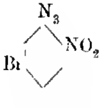
) be the most satisfactory representation of these compounds, a onviction in which we are now supported by Green and Rowe this vol., p. 897), whose preliminary announcement appeared imultaneously with our own.

The authors mentioned base their conclusion on the course ollowed by the oxidation of o-nitroamines with alkaline sodium ypochlorite. They produced the same tolufurazan oxide alike rom *p*-nitro-*m*-toluidine and *m*-nitro-*p*-toluidine, whilst from -chloro- and *p*-chloro-o-nitroanilines the same chlorobenzfurazan xide was obtained. Our inquiry depends on the decomposition f o-nitroazoimides. Having first repeated the earlier experiments ith 1-nitro-2-naphthylazoimide and 2-nitro-1-naphthylazoimide, suring ourselves that the same naphthafurazan oxide arises from oth, two bromonitrophenylazoimides:



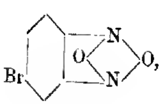
M. p. 80°.

and

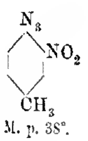


M. p. 66°.

ere prepared, and found to yield the same bromobenzfurazan xide,

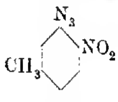


hen heated. Furthermore, from the isomeric nitrotriazotoluenes,



M. p. 38°.

and

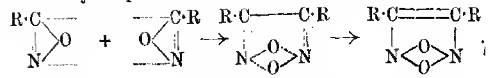


M. p. 87°.

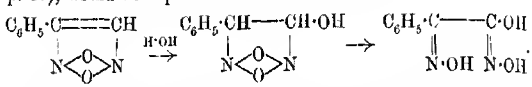
e tolufurazan oxide prepared by Green and Rowe from the nitro-oluidines has been obtained, and it seems to us that all these periments taken together place the symmetrical structure of the omatic furazan oxides on a firm basis.

Whether this conclusion is applicable also to the aliphatic compounds of Wieland and Semper cannot be stated so definitely, but ere is much in favour of extending it to these derivatives; for stance, the statement that the most general and most important urce of the dioxime "peroxides" is the polymerisation of the itrile oxides (*Annalen*, 1907, **358**, 37) involves, on the basis of e formula put forward by those authors, behaviour different on e part of one molecule from that of another, which appears

improbable, whereas according to our formula the polymerisation would be very simple:

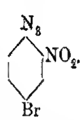


Furthermore, decomposition of diphenylglyoxime "peroxide" into phenylcarbimide (2 mols.) is more in accordance with a symmetrical structure, whilst the action of alkali on phenylfuroxan, leading to oximinobenzoylformhydroxamic acid (*loc. cit.*, p. 59), would be represented as follows:



Green and Rowe found that with hydroxylamine the furazan oxides may be reduced to the dioximes, a change which takes place also when reduction is effected with zinc dust and a limited amount of acetic acid (Forster, T., 1903, **83**, 525). We have studied the behaviour of these compounds towards hydrazine hydrate, which leads in some cases to the furazan, in others to the diamine.

EXPERIMENTAL.

4-Bromo-2-nitrophenylazoimide, 

4-Bromo-2-nitroaniline (6·5 grams) suspended in a mixture of glacial acetic acid (40 c.c.) and sulphuric acid (20 c.c.) was treated with ice and solid sodium nitrite until a clear solution was formed. Excess of nitrite having been destroyed with carbamide, aqueous sodium azide (4 grams) was added, when the substituted azoimide was precipitated in very pale yellow crystals. After recrystallisation from cold acetone diluted with water, followed by precipitation from cold benzene with petroleum, a felted mass of almost colourless needles was formed, melting at 80°:

0·1972 gave 38·3 c.c. N_2 at 13·5° and 766 mm. N=23·2.

$C_6H_3O_2N_4Br$ requires N=23·1 per cent.

The substance is freely soluble in cold benzene or acetone, less readily in methyl or ethyl alcohol, and very sparingly soluble in petroleum.

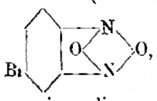
Decomposition by Heat.—In quantities of 2 decigrams, 4-bromo-2-nitrophenylazoimide was heated at 80—90°, the temperature being raised very gradually to 110° as the liberation of nitrogen

slackered. On extracting with warm petroleum (b. p. 60—80°), only a very slight tarry residue was left, the solvent depositing opaque masses of pale yellow, lustrous prisms, melting at 69°:

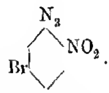
0·2004 gave 21·4 c.c. N_2 at 15° and 775 mm. N=12·9.

$C_6H_3O_2N_2Br$ requires N=13·0 per cent.

4-*Bromobenz*iso*oxadiazole oxide* (4-*bromobenzfurazan oxide*),



is freely soluble in cold organic media excepting petroleum.

5-*Bromo*-2-*nitrophenylazoimide*, 

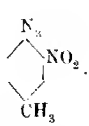
The base required for making this material was prepared by eating 2:4-dibromo-1-nitrobenzene with alcoholic ammonia during wo days at 150°, unchanged dibromonitrobenzene being removed y extracting the product several times with warm petroleum, in which 3-bromo-6-nitroaniline is only sparingly soluble. Conversion nto the substituted phenylazoimide was effected by the process used n the case of the isomeride, the pale yellow oil precipitated from he diazonium solution by sodium azide solidifying almost immediitely. The substance melts at 66°:

0·2000 gave 39·5 c.c. N_2 at 15° and 751 mm. N=22·9.

$C_6H_3O_2N_4Br$ requires N=23·1 per cent.

5-Bromo-2-nitrophenylazoimide is freely soluble in cold benzene, acetone, or ethyl acetate, and dissolves readily in warm petroleum (60—80°), separating in pale yellow, transparent plates or rectangular prisms.

Decomposition by Heat.—Proceeding as before, the substituted phenylazoimide was transformed into 4-bromobenz*iso*oxadiazole oxide melting at 69°, not depressed by admixture with the product of heating 4-bromo-2-nitrophenylazoimide.

3-*Nitro*-4-*triazotoluene*, 

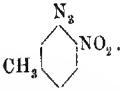
Diazotised nitrotoluidine (CH_3:NO_2:NH_2 = 1:3:4) was treated in the manner described above, when the azoimide separated as an oil, which rapidly solidified; after recrystallisation from acetone

and finally from alcohol, diluted in each case with water, it separated in long, pale yellow needles, melting at 38°:

0·1307 gave 36·0 c.c. N_2 at 24° and 764 mm. N=31·5.

$C_7H_6O_2N_4$ requires N=31·5 per cent.

Decomposition by Heat.—When heated carefully the azoimide began to effervesce at 70—75°, and decomposition became complete after raising the temperature to 110°; recrystallisation from hot petroleum (80—100°) gave a specimen of tolufurazan oxide melting at 96° (Green and Rowe give 97°).

4-Nitro-3-triazotoluene, 

The substituted azoimide was derived from diazotised nitrotoluidine ($CH_3:NO_2:NH_2$=1:4:3) in the usual manner, and after recrystallisation from cold acetone diluted with water separated in pale yellow needles melting at 87°:

0·1202 gave 33·9 c.c. N_2 at 26° and 763 mm. N=31·5.

$C_7H_6O_2N_4$ requires N=31·5 per cent.

Decomposition by Heat.—A somewhat higher temperature was required to complete this change; gas was liberated most freely at 90—100°, and 110—120° was finally attained. Some tar remained after extracting with hot petroleum (80—100°), which deposited the tolufurazan oxide melting at 96°, identical with the product from 3-nitro-4-triazotoluene.

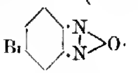
Behaviour of the Furazan Oxides towards Hydrazine Hydrate.

Benzfurazan oxide, prepared by heating *o*-nitrophenylazoimide, was treated in alcoholic solution with considerable excess of hydrazine hydrate, when the liquid became dark red; effervescence began, and became vigorous on gentle warming. After five to six hours on the water-bath the liquid remained clear on dilution, and was then evaporated to dryness; on extracting the residue with hot petroleum (60—80°) the latter deposited *o*-phenylenediamine in lustrous, rectangular plates melting at 103°. Similarly, tolufurazan oxide (m. p. 96°) gave tolylenediamine ($CH_3:NH_2:NH_2$= 1:3:4) melting at 89°, and *p*-benzoquinonedioxime "peroxide" gave *p*-phenylenediamine melting at 141°.

In the case of naphthafurazan oxide, however, arising alike from 2-nitro-1-naphthylazoimide and 1-nitro-2-naphthylazoimide, 1:2-naphthylenediamine was not produced, the product consisting of naphthafurazan (m. p. 79°), the anhydride of naphthaquinone-

dioxime (Found, N = 16·5; $C_{10}H_6ON_2$ requires N = 16·5 per cent.). This compound has a marked odour of bitter almonds, a property which has hitherto escaped notice.

*4-Bromobenz*iso*oxadiazole* (*4-Bromobenzfurazan*),



On adding hydrazine hydrate (5 c.c.) to a solution of bromobenzfurazan oxide (2 grams) in alcohol (40 c.c.) a deep red colour was developed, and gas was liberated; after being gently warmed during three to four hours, water precipitated long, yellow needles, melting at 75° after recrystallisation:

0·1473 gave 17·5 c.c. N_2 at 15° and 773 mm. N = 14·2.
$C_6H_3ON_2Br$ requires N = 14·1 per cent.

The substance has a distinct odour of menthol; it is freely soluble in most organic media, and does not reduce ammoniacal silver oxide.

ROYAL COLLEGE OF SCIENCE, LONDON,
SOUTH KENSINGTON, S.W.

CCVII.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part IV.* The Rotations of the Normal Secondary Alcohols of the Formula* $C_2H_5·CH(OH)·R$.

By ROBERT HOWSON PICKARD and JOSEPH KENYON.

SEVERAL optically active carbinols of the general formula $R^1·CH(OH)·R^2$ have already been synthesised and described (*loc. cit.*); of these, ten belong to the series of the formula

$$CH_3·CH(OH)·R$$

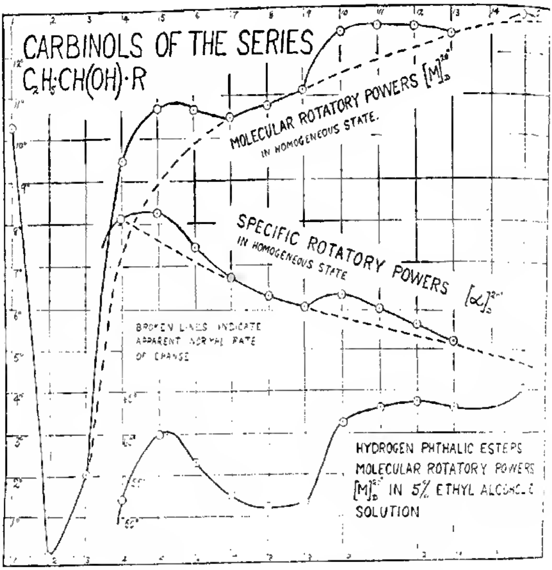
(hereafter called the "methyl" series), and eight belong to the series of the formula $CH(CH_3)_2·CH(OH)·R$ (hereafter called the "*iso*propyl" series) (where R in each case represents a normal aliphatic radicle). Another series containing thirteen similar carbinols of the formula $C_2H_5·CH(OH)·R$ having been now prepared, it is possible to contrast the rotatory powers of the members

* For Part I of this series see T., 1911, **99**, 45; Part II, T., 1912, **101**, 620, and Part III, *ibid.*, 1427.

of this "ethyl" series with those of the members of the "methyl" and "*iso*propyl" series, since the corresponding members of each series only differ from one another as regards chemical constitution in containing the methyl, *iso*propyl, or ethyl groups.

In Fig. 4 (p. 1929) it will be seen that in the "methyl" series $CH_3\cdot CH(OH)\cdot R$, where R=propyl to undecyl, the molecular rotatory powers of the carbinols in the homogeneous state (at least at the boiling points) increase regularly as the molecular weight

FIG. 1.



Number of carbon atoms in growing chain R.

and size of the growing chain R increases, whilst the figures in table I, Part II, and Fig. 3 (p. 1927) show that in the "*iso*propyl" series the molecular rotatory powers of the carbinols in the homogeneous state increase rapidly until R=butyl, the higher members of the series having molecular rotatory powers only slightly higher than, or possibly equal to, that of the member with R=butyl.

It is now found that in the homogeneous state the molecular rotatory powers of the members of the ethyl series (see table I and Fig. 1) offer a decided contrast to those of each of the other series.

They increase slowly but definitely as the growing chain R increases in size from propyl to (at least) pentadecyl, but in addition to this normal increase (indicated by the dotted line in Fig. 1), there is a further increase in the molecular rotatory power exhibited by those members of the series in which the growing chain contains 5 (or 6), 10 (or 11), and 15 carbon atoms. This exaltation from the normal increase is greater when the growing chain contains five than when it contains ten carbon atoms, and is far less pronounced in the member containing fifteen carbon atoms in the growing chain.

TABLE I.

Rotatory Powers of the Normal Secondary Alcohols of the Formula $C_2H_5 \cdot CH(OH) \cdot R$.

R. (A normal alkyl group.)	In the homogeneous state.				Dispersion.*	In 5 per cent. solution in	
	$[\alpha]_D^{20°}$.	$[M]_D^{20°}$.	$[\alpha]_{gr}^{20°}$.	$[M]_{gr}^{20°}$.	$\alpha_D/\alpha_{Hg\ green}$.	ethyl alcohol $[M]_D^{20°}$.	benzene. $[M]_D^{20°}$.
Methyl	13·87°	10·30	16·09	11·91	0·845	10·77	10·44
Ethyl	Optically inactive.						
Propyl	1·97	2·01	2·24	2·29	(0·88)‡	1·17	1·87
Butyl	8·13	9·43	9 58	11·11	0·850	11·17	10·80
Amyl	8·22	10·69	9·64	12·53	0·856	14·47	13·26
Hexyl	7·38	10·63	8 63	12·43	0·858	13·86	13·82
Heptyl	6·68	10·58	7·76	12·26	0·864	9·81	12·11
Octyl	6·25†	10·74†	7·23	12·43	0·863	10·69	12·18
Nonyl	5·97†	11·09†	6·92	12 86	0·866	11·35	12·48
Decyl	6·23†	12·44†	7·21	14·42	0·865	13·46	14·62
Undecyl	5·87†	12 56†	6·80	14·55	0·865	13·38	15·50
Dodecyl	5·53†	12·61†	6·40	14·59	0·865	12·44	15·32
Tridecyl	5·11†	12·38†	5·92	14·32	0·863	12·75	15·44
Tetradecyl.........	(Has not been prepared)						
Pentadecyl	4·77†	12·88†	5·49	14·83	0·865	12·91	16·63

* These figures represent the average value of the rotatory dispersive powers calculated at intervals of 20° from 20° to 160° (or to the boiling points of the carbinols) as given in table II.

† Values at 20° extrapolated from curves based on observations recorded on p. 1954. These carbinols melt at about or above 20°.

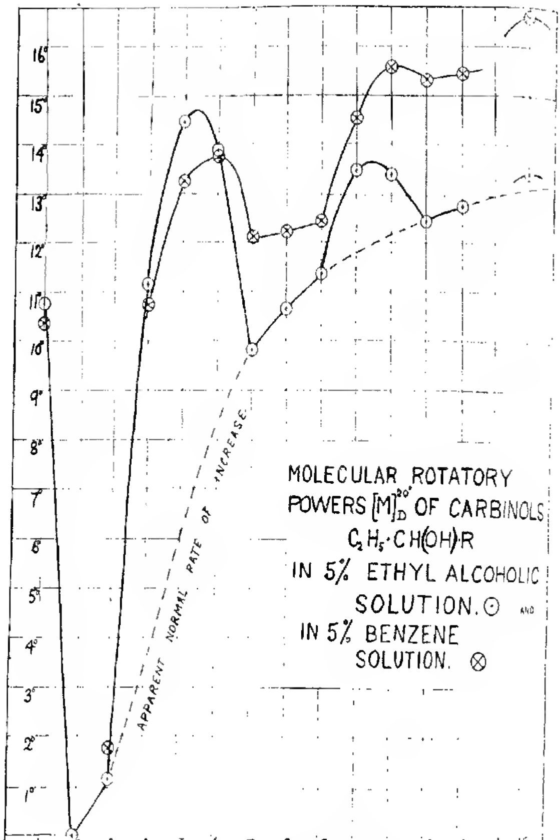
‡ See footnote, p. 1931.

Frankland has already suggested (T., 1899, 75, 368) that a maximum (or constant) rotatory power in a homologous series of optically active compounds would probably be attained when the growing chain contained five or six carbon atoms, since it is at that part of the series where it is expected from stereochemical considerations that the growing chain would all but return on itself. Our results appear to show conclusively that in the "ethyl" series, $C_2H_5 \cdot CH(OH) \cdot R$, there is a continuous gradual increase in the molecular rotatory powers as the growing chain increases, with

a further special exaltation each time that the growing chain of carbon atoms returns on itself.

When discussing some of our previous results, Frankland (T.

FIG. 2.

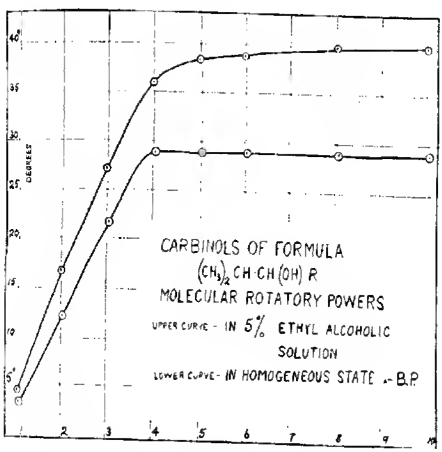


Number of carbon atoms in growing chain R.

1912, **101**, 660) suggested that some solvents like alcohol might "permit of a more unrestricted development of the rotatory effect of the homologous group (growing chain) than is the case when the

same compounds are examined in the liquid condition." This is actually the case when these carbinols are examined in ethyl-alcoholic solution. Thus, as will be seen from Fig. 2, the values of the rotatory powers of the members of the "ethyl" series follow those obtained when they were examined in the homogeneous state, but the effect due to the special stereochemical configuration of the growing chain when this contains about five or ten carbon atoms is much more pronounced. Similar results are obtained when the carbinols are examined polarimetrically in benzene solution. This same effect is also to be observed when the carbinols of the *iso*propyl series are examined in ethyl-alcoholic solution.

FIG. 3.



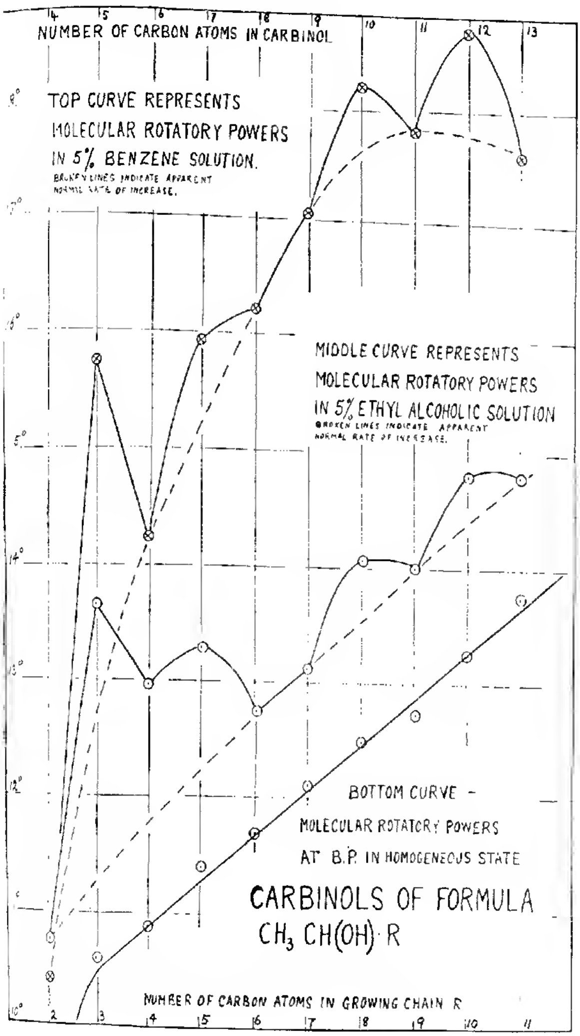
Number of carbon atoms in growing chain R.

Thus (see Fig. 3), in the homogeneous state, an approximately constant value of the molecular rotatory power is reached for the butyl member, but in ethyl alcohol it is at the amyl member that the approximately constant value of the molecular rotatory power is attained. When the members of the "methyl" series are examined in ethyl alcohol or in benzene, the values obtained for the molecular rotatory powers (Fig. 4) are at first sight very confusing. Maxima on the irregular curves will be observed corresponding with methylpropylcarbinol, methylamylcarbinol, methyloctylcarbinol, and methyldecylcarbinol, and the curves are in striking contrast to the regular curve show-

ing the values of the molecular rotatory powers determined a the boiling point of the carbinols in the homogeneous state. The maxima on these curves, corresponding with methylamyl- and methyldecyl-carbinols are, of course, to be attributed to the special configuration of the growing chain. However, adopting a different nomenclature, methylpropylcarbinol, $CH_3 \cdot CH(OH) \cdot C_3H_7$, and methyloctylcarbinol, $CH_3 \cdot CH(OH) \cdot C_8H_{17}$, can be designated pentan-β-ol and decan-β-ol. It will now be seen that the maxima corresponding with these two carbinols containing five and ten carbon atoms respectively in the molecule can be attributed to the special configuration of the *normal chain of carbon atoms comprising the whole molecule.* So that the polarimetric examination of these solutions has afforded most conclusive evidence of the special effect that a normal chain of five (or ten) carbon atoms has on the rotatory power of a compound. In the "ethyl" series $C_2H_5 \cdot CH(OH) \cdot R$, a similar effect where the compounds (as distinct from the growing chain) contain five or ten carbon atoms, has not been observed—pentan-γ-ol (diethylcarbinol) is symmetrical, and therefore optically inactive, whilst the values obtained for the molecular rotatory power of decan-γ-ol (ethylheptylcarbinol) occupy a normal position on the three curves illustrating the observations in the homogeneous state, in ethyl-alcoholic solution and in benzene solution. The results recorded in this paper appear then to afford a very striking confirmation of Frankland's suggestion made fourteen years ago. Although this was based on the then conventional idea of the rigid tetrahedron model of the carbon atom, yet it, in common with theories such as Baeyer's Strain Theory, is not upset by more modern conceptions of the carbon atom. The carbon atom can be imagined to be a sphere with valency (or combining force) radiating from the centre like "lines of force" to the surface of the sphere (Werner). The further postulation of a greater concentration of the forces about the points of contact of the sphere with a regular tetrahedron circumscribed by it would explain perhaps better than the older idea of the rigid tetrahedron model the peculiar effect of a chain containing about five carbon atoms on the rotatory power of the compound.

The opinion of the authors, expressed in Part I (p. 47, *loc. cit.*), that in a reinvestigation of the problem of the relation between rotatory power and chemical constitution it was desirable to restrict the polarimetric examinations to those of liquids in the homogeneous state is now shown to be untenable. It is obvious that some effects due to the configuration of the molecule are only to be observed in solution, and are marked at all temperatures up

FIG. 4.


NUMBER OF CARBON ATOMS IN CARBINOL
TOP CURVE REPRESENTS
MOLECULAR ROTATORY POWERS
IN 5% BENZENE SOLUTION.
MIDDLE CURVE REPRESENTS
MOLECULAR ROTATORY POWERS
IN 5% ETHYL ALCOHOLIC SOLUTION
BOTTOM CURVE -
MOLECULAR ROTATORY POWERS
AT B.P. IN HOMOGENEOUS STATE
CARBINOLS OF FORMULA
CH3 CH(OH)·R
NUMBER OF CARBON ATOMS IN GROWING CHAIN R

to the boiling point, when the compounds are examined in the homogeneous state.*

There does not appear to be any simple numerical relation between the various values obtained for the molecular rotatory powers of the members of these homologous series, and it does not seem probable from the results obtained (even after giving due weight to the obvious objection that they relate to only one class of compounds) that any such numerical relation exists between the rotatory powers of the members of any homologous series.

The following hypothesis based merely on a consideration of the space occupied by the four groups attached to the asymmetric carbon atom appears to explain the results obtained for the three series of carbinols as well as those obtained for eight series of simple esters derived from the "methyl" series of carbinols which will be described in Part V.

In a homologous series of optically active compounds represented by *Cabcd*, the usual effect of increasing the size of *d* (representing the growing chain) is to alter in a regular manner (usually to increase) the molecular rotatory power of the compounds. When the groups (or atoms) represented by *a*, *b*, and *c* occupy a relatively small space, as, for example, in the "methyl" series of carbinols, $CH_3 \cdot CH(OH) \cdot R$, the values of the molecular rotatory powers of the homogeneous compounds increase regularly with the increasing size of the chain, and only in solution are affected by the peculiar configuration of the chain, when this returns on itself.

When, however, the space occupied by the groups (or atoms) represented by *a*, *b*, and *c* is larger, the increase in molecular rotatory power as *d* increases in size may become less regular; either (i) it may be specially affected, when the chain returns on itself, as in the "ethyl" series, $C_2H_5 \cdot CH(OH) \cdot R$, or (ii) there may be a relatively large increase until *d* contains five carbon atoms with an increase of a much smaller order beyond, as, for example, in a series of esters, such as those of *sec.*-octyl alcohol with normal aliphatic acids,† in which there is a large increase in the value of the molecular rotatory power for each member of the series up to the *n*-valerate, and a still further, but relatively much smaller, increase for each member from the valerate to the palmitate; or (iii) when the space occupied by the groups *a*, *b*, and *c* is still greater, an "approximate maximum" is reached when the growing chain contains fewer than five carbon atoms, as, for

* This point has an obvious bearing on the assumed connexion between association and alteration of rotatory power in various solvents, and will be discussed in the next paper of this series.

† See Part V.

xample, for the carbinols of the "*iso*propyl" series,

$$CH(CH_3)_2\cdot CH(OH)\cdot R$$

when these are examined in the homogeneous state), and in a ries* of *n*-dodecoates of the "methyl" carbinols,

$$R\cdot CH(O\cdot CO\cdot C_{11}H_{23})\cdot CH_3,$$

n both of which the values of the molecular rotatory power increase apidly up to that for the member with R containing four carbon toms with a much smaller increment for the higher members.

Optical Dispersion.

The rotations of the carbinols of the three series have been etermined for yellow (sodium) and green (mercury) light at emperatures from 20° to 160° (or to the boiling points of the arbinols). For each carbinol the dispersion value appears to be a onstant (within the possible experimental error) over the range of emperature employed. Similar results have now been obtained by he authors in the case of ten series of compounds, so that optical ispersion may be considered generally to be independent of the emperature, as Walden has already assumed from his investigation f five esters of ricinoleic acid (*Ber.*, 1903, **36**, 781). The differences n the values of the dispersive power of the various members of a eries of homologous compounds do not run parallel with the ariations in the rotatory powers; thus, in the "methyl" series, ll the members from the propyl to the undecyl have the same ispersive power (yellow/green 0·847), whilst that for the ethyl ember is slightly less (0·840). Similar results have been obtained or the "*iso*propyl" series, each of the carbinols from the ethyl o the decyl member of this series having the same value for the ispersion (0·842), which varies from that of the methyl member; whereas in the "ethyl" series the methyl member (which is, of ourse, the ethyl member of the "methyl" series) with the value 0·810, and the propyl member with the value 0·88,† have dispersive powers varying widely from those of the butyl, amyl, and hexyl members, which have yellow/green values 0·850, 0·856, 0·858 respectively, thus approaching the constant value 0·865 given by the other (heptyl to pentadecyl) members of the series. These variations from the constant for the series are difficult to explain, but will be further discussed in a paper with Dr. T. M. Lowry, who has made some very accurate determinations of the dispersive

* See Part V.

† Owing to the low rotatory power of the carbinol this value is probably not as accurate as the others given. There is, however, no doubt that the value of dispersive power (yellow/green) is much higher than that for the other members of the series.

powers of these carbinols at 20°, the results of which agree with those obtained by the present authors over the wide range of temperature employed.

Effect of Temperature on the Rotatory Powers.

The rotatory powers of the carbinols of the "ethyl" series are affected only very slightly by an increase of temperature, except in the case of methylethylcarbinol, which, although common to both the "methyl" and "ethyl" series, possesses physical constants abnormal to each. The effect of temperature on the rotatory powers is very much less in the "ethyl" than in the "methyl" and "*iso*propyl" series; so slight is this that it is difficult (considering the possibility of experimental error) to determine definitely any singular points in the temperature-rotation curves. Table II shows the values obtained from the smoothed curves at temperatures from 20° to 160°. There do not appear to be any obvious regularities in the temperature-rotation curves. Thus, for the propyl, butyl, and amyl members of the series, the molecular rotatory powers increase with the temperature up to the neighbourhood of their boiling points; for the hexyl, heptyl, and octyl members they increase to a maximum at about 120°, 80°, and 140° respectively; for the nonyl, decyl, and dodecyl members, the rotatory powers decrease as the temperature increases up to about 130°, and then fall as the temperature rises further, whilst for the undecyl, tridecyl, and pentadecyl members they decrease slowly as the temperature increases up to 160°. In nearly all these cases the variation in the molecular rotatory powers is not much larger than the possible experimental error in their determination. A comparison of the maximum values of the expression $[M]_D^{t°}$ (as suggested by Patterson, this vol., p. 147) does not bring out any fresh regularities, at least between the limits $t° = 20°$ to 160°.

General Properties of the Optically Active Carbinols.

The members of the "ethyl" series of carbinols have not been described previously in the optically active form, except *d*-methylethylcarbinol, *d*- and *l*-ethylhexylcarbinol (see Part I., *loc. cit.*), and *d*-ethyl-*n*-amylcarbinol. The latter has been recently isolated in the laboratory of Messrs. Schimmel (Semi-Annual Reports, April, 1912, 103, and April, 1913, 82) from the by-products of low boiling point obtained in the rectification of menthol, and from this source had a rotatory power slightly lower than that of the synthetical carbinol now described.

These carbinols resemble those of the "methyl" and "*iso*propyl"

TABLE II.

Molecular Rotatory Powers for Sodium-yellow and Mercury-green Light and Dispersion Values of the Series $C_2H_5\cdot CH(OH)\cdot R$ *at Various Temperatures.*

		At 20°.	40°.	60°.	80°.	100°.	120°.	140°.	160°.
-Methylethylcarbinol	yellow	+10·02°	9·34°	8·73°	8·31°	—	—	—	—
	green	11·91	11·05	10·31	9·82	—	—	—	—
	disp.	0·842	0·845	9·847	0·846	—	—	—	—
l-Ethyl-*n*-propylcarbinol	yellow	−2·01°	2·06°	2·12°	2·22°	2·32°	2·44°	—	—
	green	2·29	2·34	2·42	2·54	2·64	2·75	—	—
	disp.	0·881	0·881	0·877	0·875	0·882	0·887	—	—
d-Ethyl-*n*-butylcarbinol	yellow	+9·43°	9·49°	9·58°	9·67°	9·78°	9·90°	10·06°	—
	green	11·11	11·18	11·26	11·38	11·50	11·63	11·83	—
	disp.	0·849	0·850	0·850	0·850	0·850	0·850	0·850	—
d-Ethyl-*n*-amylcarbinol	yellow	+10·69°	10·82°	10·95°	11·06°	11·14°	11·21°	11·24°	11·22°
	green	12·53	12·69	12·79	12·93	13·04	13·09	13·11	13·08
	disp.	0·853	0·854	0·856	0·855	0·855	0·857	0·856	0·858
l-Ethyl-*n*-hexylcarbinol	yellow	−10·63°	10·91°	11·10°	11·14°	11·15°	11·18°	11·04°	10·91°
	green	12·43	12·72	12·86	12·93	12·96	13·00	12·90	12·77
	disp.	0·856	0·858	0·863	0·861	0·860	0·859	0·856	0·854
l-Ethyl-*n*-heptylcarbinol	yellow	−10·55°	10·64°	10·66°	10·70°	10·64°	10·54°	10·49°	10·38°
	green	12·23	12·28	12·32	12·36	12·30	12·23	12·14	12·01
	disp.	0·863	0·864	0·867	0·866	0·865	0·863	0·864	0·863
l-Ethyl-*n*-octylcarbinol	yellow	−10·74°	10·86°	10·96°	10·99°	11·00°	11·00°	11·10°	10·91°
	green	13·43	12·55	12·68	12·73	12·75	12·76	12·89	12·68
	disp.	0·864	0·866	0·864	0·864	0·862	0·861	0·861	0·863

TABLE II. (*continued*).

		At 20°.	40°.	60°.	80°.	100°.	120°.	140°.	160°.
l-Ethyl-*n*-nonylcarbinol	yellow	* −11·09°	10·55°	10·33°	10·26°	10·21°	10·21°	10·33°	10·51°
	green	*12·86	12·25	11·91	11·80	11·76	11·81	11·90	12·12
	disp.	0·863	0·862	0·867	0·869	0·868	0·864	0·868	0·868
d-Ethyl-*n*-decylcarbinol	yellow	* + 12·44°	*12·35°	12·28°	12·20°	12·13°	12·11°	12·11°	12·17
	green	14·42	14·33	14·22	14·14	14·03	13·97	13·96	14·00
	disp.	0·862	0·862	0·863	0·863	0·865	0·867	0·868	0·869
l-Ethyl-*n*-undecylcarbinol	yellow	* − 12·56°	*12·37°	12·28°	12·24°	12·19°	12·19°	12·16°	12·16°
	green	*14·55	*14·35	14·23	14·22	14·21	14·19	14·16	14·10
	disp.	0·863	0·862	0·863	0·861	0·858	0·858	0·859	0·862
l-Ethyl-*n*-dodecylcarbinol	yellow	* − 12·61°	*12·41°	12·26°	12·15°	12·13°	12·10°	12·20°	12·36°
	green	*14·59	*14·32	14·15	14·07	14·04	14·02	14·12	14·30
	disp.	0·864	0·867	0·866	0·863	0·864	0·863	0·864	0·865
l-Ethyl-*n*-tridecylcarbinol	yellow	* − 12·38°	*12·34°	*12·34°	12·25°	12·11°	11·97°	11·76°	11·57°
	green...............	*14·32	*14·35	*14·29	14·20	14·01	13·81	13·61	13·43
	disp.	0·865	0·861	0·863	0·862	0·864	0·866	0·862	0·864
l-Ethyl-*n*-pentadecylcarbinol	yellow	* − 12·87°	*12·80°	*12·80°	12·79°	12·72°	12·71°	12·63°	12·31°
	green...............	*14·83	*14·80	*14·80	14·79	14·72	14·72	14·62	14·28
	disp.	0·868	0·865	0·865	0·865	0·864	0·863	0·864	0·863

* Values from extrapolated curves of densities and observed rotations. All values given in the table are read off or calculated from smoothed curves based on observations recorded on p. 1954.

series as regards immunity from "racemisation"* under many conditions (see Part II, *loc. cit.*, p. 622), whilst in general their physical properties (see table III) vary in a regular manner, except for the small breaks which occur in the regularity of the densities at the hexyl and dodecyl members (compare similar breaks in the "*iso*propyl" series and in the series of esters of *ac*-tetrahydro-2-naphthol, Parts II and III, *loc. cit.*).

The odours of the lower members of the series resemble those of the "methyl" series containing the same number of carbon atoms in the growing chain, the group R in the formulæ $CH_3\cdot CH(OH)\cdot R$

TABLE III.

Optically Active Alcohols of the Formula $C_2H_5\cdot CH(OH)\cdot R$.

	Boiling point.	Melting point.	$n_D^{20^\circ}$.†	$D_4^{20^\circ}$.	Mol. Refr. $\frac{n-1}{d}\cdot M$.	Difference for CH_2.	$D_4^{80^\circ}$.
Methylethylcarbinol ...	99°/758 mm.	—	1·3954	0·8080	36·2	7·7	—
Diethylcarbinol*	114·5°/752 ,,	—	1·4094	0·8198	43·9	7·5	—
Ethyl-n-propylcarbinol	133°/733 ,,	—	1·4141	0·8213	51·4	7·9	0·7671
Ethyl-n-butylcarbinol.	66°/18 ,,	—	1·4206	0·8227	59·3	7·7	0·7679
Ethyl-n-amylcarbinol.	76°/16 ,,	—	1·4252	0·8247	67·0	8·0	0·7711
Ethyl-n-hexylcarbinol.	97°/17 ,,	—	1·4308	0·8265	75·0	7·9	0·7796
Ethyl-n-heptylcarbinol	108°/15 ,,	—	1·4336	0·8272	82·9	7·7	0·7798
Ethyl-n-octylcarbinol..	117°/16 ,,	17°	1·4367	0·8295	90·6		0·7827
Ethyl-n-nonylcarbinol	130°/15 ,,	25	—	—	—	—	0·7833
Ethyl-n-decylcarbinol.	139°/12 ,,	32	—	—	—	—	0·7865
Ethyl-n-undecylcarbinol	146°/10 ,,	38	—	—	—	—	0·7885
Ethyl-n-dodecylcarbinol	168°/14 ,,	45	—	—	—	—	0·7921
Ethyl-n-tridecylcarbinol	152°/4 ,,	50	—	—	—	—	0·7907
Ethyl-n-pentadecylcarbinol	172°/2 ,,	56	—	—	—	—	0·7858

* Optically inactive.

† Determined with a Féry refractometer and correct to about ±0·0002.

and $C_2H_5\cdot CH(OH)\cdot R$ seemingly being the portion of the molecule to which the characteristic odour is due. Beyond the member with R = *n*-decyl the odours are increasingly faint, ethyl-*n*-pentadecylcarbinol being practically odourless. No marked difference in odour between the optically active and inactive forms was observed in any case. The carbinols, when oxidised with chromic acid, readily yield in a pure state the ketones of the general formula $C_2H_5\cdot CO\cdot R$, which form semicarbazones in the usual way. The constants of these compounds are given in table IV, and differ

* It is very doubtful if any of these optically inactive carbinols exist in the liquid state as racemates (see investigations on the viscosity of several of these carbinols by Thole, this vol., p. 19).

in several instances from those previously recorded in the literature. The semicarbazones of the series $C_2H_5 \cdot CO \cdot R$ all crystallise readily from aqueous ethyl alcohol, but in the case of the higher members of the series melt at about the same temperature, and therefore, like the semicarbazones of the series $CH_3 \cdot CO \cdot R$, are of little use for the characterisation of the ketones.

TABLE IV.

Ketones of the General Formula $C_2H_5 \cdot CO \cdot R$.

Name of ketone.	Melting point.*	Boiling point.	Semicarbazone, Melting point.†
Ethyl methyl	—	78·6°	135—136°
Diethyl	—	101°	139
Ethyl *n*-propyl	—	123°	112°
Ethyl *n*-butyl	—	149—150°	99—100°
Ethyl *n*-amyl	—	165—166°	112°
Ethyl *n*-hexyl	—	185—186°	111°
Ethyl *n*-heptyl	—	211°	100—101°
Ethyl *n*-octyl	—	227°	89°
Ethyl *n*-nonyl	19°	134°/18 mm.	87°
Ethyl *n*-decyl	25°	140°/17 ,,	90°
Ethyl *n*-undecyl	33°	148°/10 ,,	89°
Ethyl *n*-dodecyl	38°	174°/20 ,,	90·5°
Ethyl *n*-tridecyl	40—41°	184°/17 ,,	86°
Ethyl *n*-pentadecyl	50°	198°/14 ,,	76°

* Determined by "cooling curve" method.

† These melting points, which were determined in a capillary tube, in several cases vary slightly according to the rate of heating. The figures given were obtained when the rate of heating was slow.

EXPERIMENTAL.

The experimental work has been carried out on similar lines to those described in Parts I to III. The externally compensated carbinols have been synthesised either by Grignard reactions or by the reduction of the corresponding ketones. The formation of a secondary alcohol by the interaction of a magnesium alkyl haloid and a normal aldehyde, R·CHO, proceeds quite smoothly for aldehydes with R containing at least up to sixteen carbon atoms, but takes place only to a slight extent if the normal alkyl group is larger than *n*-propyl. The ketones were prepared (like those described in Parts I and II) by the catalytic decomposition (according to Senderens' method, *Compt. rend.*, 1909, **149**, 995) by contact with heated thorium oxide of mixtures of the required acids, these being, except where otherwise stated, the pure acids supplied by Kahlbaum. The thorium oxide was placed in a transparent silica "combustion" tube, the average yield from the process being apparently slightly better than when a Jena glass tube is used, whilst the convenience in working is much greater

It is noteworthy that, whilst the hydrogen phthalic esters of the "methyl" series are easily resolved by the fractional crystallisation of the brucine salts, the corresponding compounds of the "ethyl" series (like those of the *iso*propyl series) are in most cases more readily resolved by the aid of strychnine, as in several cases brucine appears to form a "partly racemic" salt, which is less soluble than either the *l*B*l*A or *l*B*d*A salt. The experimental results agree well with one another, so that it has not been thought necessary to publish the large mass of analytical details. Each stage of the processes described below has been checked by analysis, but all details, for example, of the titration of the acid esters with alkali, of the combustions of the semicarbazones, and of the alkaloidal salts, etc., and of the determination of the rotatory powers of the successive crops in the resolutions, have been omitted from the description. Both the dextro- and lævo-rotatory forms of the carbinol have been obtained only in a few cases. The completeness of the resolutions has been to some extent assured by the following method. A quantity of the alkaloidal (generally strychnine) salt has been obtained with a rotation and melting point which remained unaltered by further recrystallisation. The mother liquors were then carefully worked up, and the salt thus obtained was subjected to another series of crystallisations. The resolution was deemed complete when the second lot of salt obtained in this manner had the same constants as the first lot. In each case as the strychnine salts are not always very definite compounds, the esters from each lot were prepared and examined separately in the polarimeter.

Preparation of the Hydrogen Phthalic Esters.

The hydrogen phthalic esters of the carbinols (see table V) were prepared by the following method. Equimolecular proportions of carbinol and phthalic anhydride are heated at 110—120° for about ten hours. The product is dissolved in very dilute sodium carbonate solution, and very carefully purified from non-acid substances by repeated extraction with ether. The solution, which when working up 100 grams of carbinol would amount to about 6 litres, is completely freed from dissolved ether by blowing a current of air through it for some hours. Then after the addition of an excess of hydrochloric acid the hydrogen phthalate is either drained off and dissolved in chloroform or at once extracted with that solvent. The chloroform solution is washed repeatedly with water, and carefully dried with recently fused calcium chloride, a process which removes all but mere traces of phthalic acid. The chloroform is then completely removed by distillation on a water-

bath, the last traces under diminished pressure, and the hydrogen phthalate (if solid) crystallised from petroleum of low boiling point. In most cases scrupulous adherence to these conditions is necessary to ensure the success of the subsequent resolution, which largely depends on the purity of the hydrogen phthalate.*

TABLE V.

The Hydrogen Phthalic Esters of the Carbinols, $C_2H_5\cdot CH(OH)\cdot R$

Hydrogen phthalate of carbinol with R=	Melting point of optically		Rotations in			
			Chloroform.		Ethyl alcohol.	
	Inactive.	Active.	$[\alpha]_D$.	$[M]_D$.	$[\alpha]_D$.	$[M]_D$.
n-Propyl	76—77°	73—74°	4·18°	10·45°	3·77°	9·42
n-Butyl	53—54	47—48	16·65	43·95	19·82	52·3
n-Amyl	62—63	66—68	17·06	59·7	21·67	60·2
n-Hexyl	47—49	54—55	14·12	41·2	19·45	56·8
n-Heptyl	Oil	32—33	12·67	38·8	17·30	52·9
n-Octyl	Oil	Oil	11·90	38·1	16·10	51·5
n-Nonyl	31—32	25	11·82	39·5	15·60	52·1
n-Decyl	46—47	34—35	12·84	44·7	17·71	61·6
n-Undecyl ...	58—60	36—37	13·79	49·9	17·43	63·1
n-Dodecyl ...	54—55	46—47	13·16	49·5	16·98	63·8
n-Tridecyl ...	51—52	51	12·55	49·0	16·47	63·2
n-Pentadecyl.	39—41*	34—35	12·16	50·8	15·62	65·3

* Not quite pure.

In all the determinations of the rotatory power of solutions recorded in this paper the material stated, usually about 1 gram, was made up to 20 c.c. at 20° with the solvent and the solution examined at 20° in a 2-dcm. tube.

Methylethylcarbinol (sec.-*Butyl Alcohol*), $C_4H_{10}O$.

The preparation of *d-sec.*-butyl alcohol has been described briefly in Part I. Large quantities being required for this and other work, the methods have been modified as follows: Bright magnesium turnings (72 grams) are placed in a flask (capacity, 2 litres), and covered with ether † (250 c.c.). The flask is fitted with an inverted condenser, and a solution of dry ethyl bromide (340 grams), dissolved in an equal volume of ether, is added gradually, the mixture being shaken vigorously during the whole operation, which occupies about two hours. The flask is then placed in a large pneumatic trough standing on wooden rockers, and packed round with a mixture of ice and salt. A solution of acetaldehyde (150 grams) in twice its volume of ether is then slowly run in to

* It is thought desirable to emphasise this point as want of purity of the hydrogen phthalate appears to be the cause of failure on the part of some investigators to repeat resolutions previously described.

† Commercial ether which has been washed successively with concentrated sulphuric acid, water, a solution of sodium hydroxide and water, dried over calcium chloride, and distilled over phosphoric oxide.

he mixture from a tap funnel during the course of two hours, whilst the contents of the flask are agitated by moving the trough. The mixture is allowed to remain overnight, and then the uncombined acetaldehyde and about two-thirds of the ether are removed by distillation, the flask being placed in a bucket of water warmed to 45°. One operator can conveniently control simultaneously three series of such operations. The products from nine lots of material are poured with constant stirring into a large tank containing about 12 litres of a mixture of a saturated solution of ammonium chloride and crushed ice. The ethereal solution is then syphoned off, and the remaining liquid placed in flasks (capacity 5 litres), through which a current of steam is blown so long as the distillate smells of the alcohol. The distillates are collected together, and the alcohol concentrated by a repetition of the last operation. The ether in the syphoned liquid is removed by distillation, and the alcohol purified by distillation in a current of steam. The combined distillates are then saturated with sodium chloride, and extracted five times with ether. The ethereal extracts are now dried with several successive lots of recently ignited potassium carbonate, and then distilled very slowly through a long and efficient fractionating column. This last operation needs to be repeated four times, owing to the difficulty of separating ether and sec.-butyl alcohol. The average yield of the crude *sec.*-butyl alcohol (the fraction boiling between 85° and 101°) is well represented by that obtained from a batch of nine lots of material which amounted to 1265 grams.

The hydrogen phthalic ester is prepared by the method described on p. 1937, except that the mixture of the crude alcohol and phthalic anhydride is heated on a water-bath for about twelve hours. The amount of pure hydrogen phthalic ester obtained from the 1265 grams of crude alcohol mentioned above amounted to 3204 grams.

The resolution of methylethylcarbinol in large quantities is most easily carried out by a method which is illustrated by the details of one such resolution: The pure *sec.*-butyl hydrogen phthalate (965 grams) was dissolved in warm acetone (4 litres), and after the addition of anhydrous brucine (1738 grams), kept at about 40° for an hour. The solution was then filtered from undissolved brucine and concentrated, the flask being placed in a water-bath, and about 950 c.c. of acetone distilled off. After remaining for some hours in the ice-chest, the crop of crystals (A) was collected, whilst the filtrate (3000 c.c.) was concentrated further, and yielded another crop (A_1), the filtrate from which, when acidified in the manner described in Part I (p. 62), gave 260 grams of the hydrogen

phthalic ester with $[\alpha]_D -20.0°$ in ethyl alcohol. Crop A was recrystallised from 3 litres of acetone, giving crop B and the crop A_1 from the mother liquor of crop B giving crop B_1. Crop B was then recrystallised five times (crops C, D, E, F, G) from methyl alcohol, 1200 c.c. of solvent being used for each operation, since the solubility of salt decreases at about the same rate as the size of the crops; thus crop D weighed 1 kilo. and crop G 680 grams. Crop B_1 was then recrystallised successively from the mother liquors of crops C to G, and then a further six times from fresh methyl alcohol, the yield of salt being 180 grams. The total yield of salt (860 grams) was hydrolysed in the usual manner, and gave 276 grams of the pure *d-sec.*-butyl hydrogen phthalate,* with $[\alpha]_D +38.44°$ in ethyl alcohol. To obtain the alcohol from the ester the best procedure (giving a yield of 85 per cent.) is as follows: The ester (1 mol.) is dissolved in water containing sodium hydroxide ($2\frac{1}{2}$ mols.), the solution warmed for a few minutes, and the alcohol removed by a current of steam. The alcohol is separated after the addition of potassium carbonate to the distillate, and dried by treatment with successive lots of freshly-ignited potassium carbonate, and finally with barium oxide. It then boils constantly at 99°/760 mm., and has the rotation previously recorded (see Part I, 64).

Owing to the special interest attaching to this *d*-methylethyl-carbinol as the optically active alcohol of simplest constitution, further experiments were carried out to obtain the pure *l*-alcohol, so that other evidence as to the completeness of the resolution might be obtained.

The portions of ester of highest lævorotatory power (approximately $[\alpha]_D -20°$ in ethyl alcohol) were collected from several preparations of the *d*-alcohol, and converted into the acid potassium salt (see Part I, p. 59), which was then crystallised four times from acetone. This process did not alter the lævorotation of the ester, but the partly lævorotatory alcohol obtained from it was otherwise in a high state of purity. This was then converted into the hydrogen succinic ester, which gave a crystalline *cinchonidine* salt very soluble in organic solvents. This salt after five recrystallisations from a small quantity of acetone was obtained as small, transparent prisms melting at 54–55°, had $[\alpha]_D -85.03°$ in ethyl alcohol, and was unaltered in rotatory power after further recrystallisation. The *hydrogen succinic ester* obtained from this

* The rotation of this ester in chloroform, which is pure and recently distilled, is much higher ($[\alpha]_D +40.51°$) than the value ($[\alpha]_D +33.54°$) given in Part I. The rotations of this and other phthalic esters, when determined in chloroform solution, vary greatly with the purity of the solvent.

salt was a clear mobile oil, which had $[\alpha]_D$ $-12·50°$ in chloroform. When hydrolysed in the manner described for the corresponding *d*-hydrogen phthalic ester it gave the pure l-sec.-*butyl alcohol*, which in a 25 mm. tube had α_D $-2·70°$, the corresponding value obtained for the *d-sec.*-butyl alcohol in a 100 mm. tube being α_D $-10·83°$.

Methylethylcarbinol appears to have abnormal values for certain physical constants; thus, working with a sample of the *d*-alcohol prepared by us, Dunstan and Thole (compare this vol., p. 127) obtained abnormal values for log viscosity, whilst as recorded in Part II (p. 626) Dr. T. M. Lowry obtained a value for the optical dispersive power (Hg^{violet}_{green} 1·662) differing from the constant value (1·651) which he obtained for the other members of the "methyl" series. Suspicion having arisen that these anomalies might be due to the hygroscopic character of the alcohol and the presence of traces of water, the following experiments were carried out to test the point.

A series of polarimetric readings with the purest *d*-alcohol were made in a jacketed tube, through which warm water circulated. The successive readings in a 100 mm. tube were for $\alpha_{Hg\ green}$ at 20°, −13·02°; at 30°, 12·33°; at 49°, +11·29°; at 44°, +11·55°; at 49°, +11·28°; at 44°, +11·60°; at 65°, +10·51°; at 74°, +10·27°; at 83°, +9·90°; at 90°, +9·70°; and at 96°, +9·48°; whilst for α_D the readings taken at the same time were at 20°, −10·94°; at 29°, +10·46°; at 55°, +9·31°; at 41·5°, +9·88°; at 38°, +10·01°; at 61°, +9·04°; at 80°, +8·46°; at 73·5°, +8·68°; at 68°, +8·93°; at 95°, +8·12°; at 88°, +8·26°. The values were plotted, and from the smoothed curves the following values of the dispersive power $\alpha_D/\alpha_{Hg\ green}$ were obtained: at 20°, 0·842; at 40°, 0·845; at 60°, 0·847; at 80°, 0·846; at 90°, 0·846, the mean being 0·845. This sample was then allowed to remain for three days over barium oxide, and then re-examined in the polarimeter, with the result that all the new readings were found to lie on the curves previously obtained. One per cent. of water was next added to the sample, and the following readings obtained: for $\alpha_{Hg\ green}$ at 19·5°, +12·18°; at 30·5°, +11·73°; at 35°, +11·38°; at 47°, +10·81°; at 59°, +10·37°; at 66°, +10·03°; at 78°, +9·72°; at 82°, +9·62°; at 86°, +9·50°; for α_D at 19·5°, +10·17°; at 44°, +9·26°; at 38°, +9·46°; at 91·5°, +7·86°; at 81°, +8·13°; at 72°, +8·37°; at 63°, +8·62°, whence the following values for the dispersive power were calculated; at 20°, 0·835; at 40°, 0·840; at 60°, 0·842; at 80°, 0·841; at 90°, 0·840, the mean value being 0·840. *sec.* Butyl alcohol appears to form with water a binary mixture, which boils at about 94°. The apparent

molecular weight of the alcohol in a 3 per cent. aqueous solution as measured by the depression of the freezing point was 75·8 (calculated 74). Equimolecular proportions of the alcohol and water are quite miscible; such a mixture when examined in the polarimeter in a 100 mm. tube gave α_D^{21} $+7·29°$, $\alpha^{21}_{Hg\ green}$ $+8·66°$, whence the dispersion value is 0·842. After three hours the polarimetric reading was $\alpha^{19}_{Hg\ green}$ $+8·75°$, after five days α_D^{19} $+7·36°$, after one month $\alpha^{19·5}_{Hg\ green}$ $+8·76°$, $\alpha^{19·5}_{Hg\ violet}$ $+14·52°$, whence the optical rotatory dispersion mercury violet/green is 1·657°. Further polarimetric readings of a pure sample of *d-sec.*-butyl alcohol gave, in a 2-dcm. tube, α^{20}_{violet} $+42·26°$ and α^{20}_{D} $+25·52°$, whence the rotatory dispersion is 1·656. It therefore seems certain that the value of the rotatory optical dispersion of *sec.*-butyl alcohol, although different from the normal values shown by other members of both the "methyl" and "ethyl" series, is not appreciably affected by traces of water.

Ethyl n-*propylcarbinol*, $C_6H_{14}O$.

The crude carbinol was prepared in the usual manner by the interaction of magnesium *n*-propyl chloride and propaldehyde. The yield from twice the gram-molecular quantities was 62 grams of the crude alcohol boiling at 130—140°.

Resolution.—The optically inactive hydrogen phthalic ester (97 grams) in the form of the hard rhombs (m. p. 76—77°), in which it crystallises from light petroleum, was dissolved in acetone (about 2 litres), and the solution heated to about 40° for half-an-hour with brucine (153 grams), filtered, concentrated to about 500 c.c., and allowed to remain overnight in the ice-chest. The crystalline salt was then collected, and the process of crystallisation repeated several times, increasingly smaller amounts of solvent being employed. After four more such crystallisations, 52 grams of the *brucine* salt were obtained in hard and transparent, prismatic rods, melting at 132—133°, and with $[\alpha]_D$ $-8·92°$ in ethyl alcohol. To this salt were added a further 23 grams (with $[\alpha]_D$ $-8·70°$), obtained by working up all, but the first, mother liquors in the manner described for the strychnine salts of the dextrorotatory hydrogen phthalates of ethyl- and *n*-amyl-*iso*propylcarbinols (Part II, p. 632), six crystallisations being carried out and fresh solvent employed for the last three. These 75 grams were once more recrystallised from acetone, and the salt with $[\alpha]_D$ $-8·91°$ decomposed in the usual manner (see Part I, p. 61). The lævorotatory *hydrogen phthalic ester* (26 grams) crystallised from light petroleum in small, prismatic needles, melted at 73—74°, and had $[\alpha]_D$ $-4·12°$ in chloroform and $[\alpha]_D$ $-3·75°$ in ethyl alcohol. The pure ester (22 grams) was dissolved in a hot aqueous solution of

potassium hydroxide (14 grams), and the l-*ethyl*-n-*propylcarbinol* removed by a current of steam. After extraction with ether in the usual manner, there were obtained 7·7 grams, boiling at 133—134°/733 mm. The first mother liquor from the crystallisation of the brucine salt was decomposed, and the ester (18 grams) with $\alpha]_D$ + 2·3° in ethyl alcohol converted into the strychnine salt in the usual manner (Part II, p. 632), chloroform and ethyl alcohol being the solvents employed. After five crystallisations the pure *strychnine* salt (11 grams) was obtained. The salt melted at 191—192°, had $[\alpha]_D$ −21·26° in chloroform, and, when decomposed in the usual manner, yielded the pure dextrorotatory *ester*, which, when crystallised from light petroleum, melted at 73—74° and had $[\alpha]_D$ +4·18° in chloroform and $[\alpha]_D$ +3·77° in ethyl alcohol. Equal amounts of the *d*- and *l*-esters were dissolved in light petroleum, and the solution seeded with the optically inactive ester, when the resulting crop of crystals melted at 75—76°. The *d*-carbinol boiled at 133—134°/733 mm., and in a 25 mm. tube gave α_D^{19} + 0·45°. The carbinol, recovered from the esters with lower rotations, was oxidised by warming gently with a solution of chromic acid, and yielded ethyl *n*-propyl ketone. This boiled at 122—124°, and formed a semicarbazone, which separates from ethyl alcohol in long, prismatic needles, and melts at 112°.

Ethyl-n-*butylcarbinol*, $C_7H_{16}O$.

The material required for the preparation of the optically active carbinol was obtained by the reduction of the corresponding ketone. The latter was prepared by passing a mixture of *n*-valeric (150 grams) and propionic (450 grams) acids through a silica tube heated to 400° and containing thorium oxide. The unchanged acids were collected and passed through the tube again, the total yield of crude ketone boiling at 147—148° being 105 grams. This ethyl *n*-butyl ketone was reduced in moist ethereal solution by finely-divided sodium, and gave 95 grams of the crude ethyl-*n*-butylcarbinol boiling at 150—152°. This carbinol, when treated with phthalic anhydride, gave 173 grams of the hydrogen phthalic ester, which crystallises from light petroleum in slender needles melting at 53—54°. This ester (151 grams) was converted into the *strychnine* salt by heating its solution in methyl alcohol with the alkaloid (190 grams). The pure salt crystallises in hard, lustrous prisms, melts at 176°, and has $[\alpha]_D$ −24·31° in chloroform. The first five crystallisations from fresh lots of methyl alcohol gave 9·5 grams of the pure salt, whilst the second crop from the second mother liquor was recrystallised from the succeeding three filtrates and four more times from fresh lots of solvent,

yielding a further 10 grams of the salt. The *esters* obtained from the crops of pure salt weighed 4·5 and 3·5 grams respectively, and had $[\alpha]_D$ +16·53° and +16·65° in chloroform. The resolution was repeated with 82 grams of the inactive ester, and 9 grams of the active ester (with $[\alpha]_D$ +16·24° in chloroform) obtained. The *hydrogen phthalic* ester of *d*-ethyl-*n*-butylcarbinol crystallises readily from light petroleum in lustrous, prismatic needles, melts at 47—48°, has $[\alpha]_D$ +19·82° in ethyl alcohol, and is easily hydrolysed by potassium hydroxide. The dextrorotatory carbinol was isolated in the usual manner, and boiled at 66°/18 mm. The strychnine salts of the *d*- and *l*-esters do not vary very widely in solubility in methyl alcohol, the first mother liquor in the first resolution described above giving an ester only having $[\alpha]_D$ −2·0° in chloroform. Two series of experiments were carried out, in which strongly dextrorotatory and lævorotatory hydrogen phthalic esters were converted into the corresponding brucine salts. When either lot of brucine salt was recrystallised several times from acetone it was found that the least soluble portion in each case gave an ester, which was optically inactive. It thus appears that brucine forms a partly racemic salt with the hydrogen phthalic ester of ethyl-*n*-butylcarbinol.

Ethyl-n-*amylcarbinol*, $C_8H_{18}O$.

The optically inactive carbinol was prepared in a similar manner to that described for the corresponding *n*-butyl compound. A mixture of 145 grams of *n*-hexoic and 180 grams of propionic acids gave 124 grams of crude ethyl *n*-amyl ketone boiling between 160° and 170°. From this, 106 grams of the crude carbinol boiling at 168—172°/753 mm. were obtained and 197 grams of the corresponding hydrogen phthalic ester.

The resolution of the hydrogen phthalic ester of ethyl-*n*-amylcarbinol by the fractional crystallisation of the strychnine salt from methyl alcohol proceeds fairly readily. The ester (137 grams), which had been obtained from light petroleum in large, transparent plates melting at 62—63°, was dissolved in 1½ litres of methyl alcohol, in which the strychnine (164 grams) was suspended. The resolution was carried out as in the case of ethyl-*n*-butylcarbinol. The pure *strychnine* salt of the *d*-ester, obtained after seven crystallisations, melted (when heated slowly) at 164—166°, and had $[\alpha]_D$ −24·41° in chloroform. Systematic working up of the filtrate (fourteen further crystallisations) gave more of the salt, which with the former lot yielded 16·5 grams of the pure *d*-ester. This crystallised from light petroleum in hard, vitreous plates, melted at 66—68°, and had $[\alpha]_D$ +16·96° in

hloroform and $[\alpha]$ +21·67° in ethyl alcohol. The *d-carbinol* btained in the usual manner boiled at 76°/16 mm. The *l*-ester ecovered from the first mother liquor had $[\alpha]_D$ −7·0° in chloroform, but neither from this nor from the optically inactive ester ould the pure *l*-ester be obtained by ten crystallisations of the rucine salt from acetone. This alkaloid forms a stable partly acemic salt, which softens at 102—107°, melts at 121—123°, has $[\alpha]_D$ −9·01° in ethyl alcohol, and when decomposed yields the nactive ester melting at 61—63°.

Ethyl-n-hexylcarbinol, $C_9H_{20}O$.

The resolution of this carbinol has been already described in Part I (*loc. cit.*). It has been repeated, using a hydrogen phthalic ester, which was prepared from a sample of the carbinol obtained by the reduction of the corresponding ketone. Analogous results were obtained, various lots of ester from the pure brucine, *strychnine* and cinchonidine salts having respectively $[\alpha]_D$ +14·03°, +14·12°, and −13·73° in chloroform.* The strychnine salt crystallises from methyl alcohol in prisms, melts at 146—147°, and has $[\alpha]$ −23·41°. The carbinols obtained from these different lots of esters had rotatory powers identical with those previously described (*loc. cit.*).

Ethyl-n-heptylcarbinol, $C_{10}H_{22}O$.

Ethyl n-heptyl ketone, $C_{10}H_{20}O$, is readily prepared by the Senderens catalytic process. A mixture of *n*-octoic (200 grams) and propionic (400 grams) acids passed twice over thoria heated to 400° gave 146 grams of the ketone, which boiled at 211°. It is much more readily reduced by sodium in moist ethereal solution than in moist ethyl-alcoholic solution. From the above quantity of ketone 130 grams of the corresponding *ethyl-n-heptylcarbinol*, boiling at 213°, were obtained. The oily *hydrogen phthalic* ester of this could not be made to crystallise even when cooled to a low temperature, and seeded with a speck of the lævorotatory form described below. It is readily resolved by means of strychnine, the details of one experiment being as follows: The ester (157 grams) and strychnine (171 grams) were dissolved in chloroform, which was then removed as completely as possible on a water-bath, the resulting paste being rapidly dissolved in acetone (1 litre) previously heated to its boiling point. The crop (*A*) of crystals (m. p. 119—122°) deposited when this solution cooled was recrystal-

* The esters described in Part I (*loc. cit.*) had $[\alpha]_D$ +13·78° and −13·62° in chloroform. An obvious miscalculation of the molecular rotatory powers recorded in Part I, table IX, is corrected in table V of this paper (see p. 1938).

lised by a similar process, giving crop *B*, which was then recrysta lised eight times from fresh lots of methyl alcohol, 72 grams of the pure *strychnine* salt of the *l*-ester being obtained. The salt melts at 140—141°, and has $[\alpha]_D$ $-18{\cdot}18°$ in pure chloroform. The mother liquors from crops *A* and *B* were decomposed, and gave respectively 52 grams and 19 grams of ester with $[\alpha]_D$ $+6{\cdot}4°$ and $+4{\cdot}2°$ in pure chloroform. The 72 grams of the above-mentioned salt and a further small amount obtained by systematically working up the alcoholic mother liquors gave 25 grams of the *l*-ester which solidified on cooling to a fairly hard, crystalline mass. This was pressed out on a porous tile, when it melted at 32—33°, and had $[\alpha]_D$ $-17{\cdot}30°$ in ethyl alcohol and $-12{\cdot}67°$ in chloroform. Samples of the ester with $[\alpha]_D$ in chloroform about $+5°$ and $-3°$ respectively formed brucine salts, which crystallised readily from acetone. Each lot when crystallised repeatedly from acetone gave the same (partly racemic) *brucine* salt, which melted at 112—114°, had $[\alpha]_D$ $-7{\cdot}46°$ in ethyl alcohol, and from which an optically inactive and oily ester was obtained. l-*Ethyl*-n-*heptylcarbinol* is readily obtained by the hydrolysis of the *l*-ester in the usual manner, is volatile in a current of steam, and boils at 108°/15 mm.

Ethyl-n-*octylcarbinol*, $C_{11}H_{24}O$.

Two separate mixtures of *n*-nonoic (150 grams) and propionic (460 grams) acids when treated by the Senderens process, gave yields of *ethyl* n-*octyl ketone*, $C_{11}H_{22}O$, amounting to 108 and 105 grams respectively. This crude ketone boiled at 223—228°, and was not readily reduced by sodium in boiling ethyl alcohol. Thus, 105 grams of the ketone, when reduced by these means in the usual manner, only gave 50 grams of crude ethyl-*n*-octylcarbinol, which boiled at 225—230°, and was readily converted into the oily *hydrogen phthalic* ester. This was easily resolved by the aid of strychnine. A mixture of the ester (116 grams) and strychnine (122 grams) was dissolved in boiling methyl alcohol, and the crude salt obtained from this solution crystallised six times from fresh amounts of the solvent. The melting point (142—143°) and the rotatory power ($[\alpha]_D$ $-16{\cdot}75°$ in chloroform) of the strychnine salt thus obtained were unaltered by three further recrystallisations. The oily *l*-ester from the salt thus purified amounted to 16·5 grams, and had $[\alpha]_D$ $+16{\cdot}10°$ in ethyl alcohol, and $[\alpha]_D$ $-11{\cdot}90°$ in chloroform. l-*Ethyl*-n-*octylcarbinol* is volatile with steam, boils at 117°/16 mm., and when cooled sets to a mass of crystalline needles, which melt at 17°. Samples of the ester having low dextro- and lævo-rotatory powers formed brucine salts, which were very soluble in acetone. These salts, after several recrystallisations, became less

...uble, and yielded specimens of ester which were almost optically inactive. An ester of very low rotatory power yielded a carbinol, which boiled at 229°.

Ethyl-n-*nonylcarbinol*, $C_{12}H_{26}O$.

Ethyl-*n*-nonylcarbinol was prepared by the action of magnesium ethyl bromide on *n*-decaldehyde. The required aldehyde was obtained by the general method discovered independently by Le Sueur (T., 1904, **85**, 827) and Blaise (*Compt. rend.*, 1904, **138**, 697). Three hundred grams of *n*-undecoic acid * were brominated with 516 grams of bromine and red phosphorus in the usual manner, 442 grams of *α-bromo*-n-*undecoic acid*, $C_{11}H_{21}O_2Br$, boiling at 178–183°/14 mm., and melting at 10°, being obtained.† The bromo-acid (776 grams) was dissolved in $6\frac{3}{4}$ litres of water, $1\frac{1}{2}$ kilos. of commercial sodium hydroxide were added, and a rapid current of superheated steam was blown for twenty hours through the mixture, which was placed in a large and deep earthenware vessel (an ordinary domestic "bread mug"). After acidification, the solid obtained was crystallised from light petroleum, and gave 570 grams of the pure *α-hydroxy*-n-*undecoic acid*, $C_{11}H_{22}O_3$, which melts at 74°. The hydroxy-acid was rapidly distilled in portions of 15 grams from small flasks under ordinary pressure, and the products redistilled under diminished pressure, the whole series of operations being repeated with the portions boiling above 110°/14 mm. In this manner 88 grams of *n*-decaldehyde (b. p. 93° 13 mm.) were obtained from 240 grams of the hydroxy-acid. The freshly distilled aldehyde (88 grams) was then added in the

* *Preparation of undecoic acid.*—A large quantity of *n*-undecoic acid was prepared for the synthesis of ethyl-*n*-nonyl- and ethyl-*n*-decyl-carbinols. The details of the preparation are as follows: The slow distillation under 40 mm. pressure of 18 kilos. of crude castor oil in half-kilo. lots gave, after careful fractionation of the products, 1180 grams of *n*-undecenoic acid and 1605 grams of *n*-heptaldehyde. The acid was esterified by the Fischer—Speier method (*Ber.*, 1895, **28**, 3252), using 4540 grams of 96 per cent. ethyl alcohol and 394 grams of concentrated sulphuric acid. After careful fractionation 1162 grams of ethyl *n*-undecenoate were obtained and reduced catalytically in an atmosphere of hydrogen in the presence of finely divided nickel heated to 170° (Darzens, *Compt. rend.*, 1907, **144**, 329). The ester was passed four times over the nickel (the refraction being practically unaltered by the fourth operation), was then well shaken with one per cent. solution of potassium permanganate, dried in the usual way and again carefully fractionated, 975 grams of ethyl undecoate (b. p. 110°/20 mm.) being obtained. When hydrolysed, the yield of undecoic acid, which melted sharply at 28° and boiled at 179°/28 mm., amounted to 774 grams. Further quantities of this acid were prepared in a similar manner from undecenoic acid obtained from Kahlbaum.

† In a second preparation, 434 grams of the bromo-acid were obtained from 346 grams of *n*-undecoic acid.

usual manner to a slight excess of magnesium ethyl bromide, and gave 85 grams of *ethyl*-n-*nonylcarbinol*, which boils at 133°/14 mm., and when cooled sets to a gelatinous, microcrystalline mass, melting at 12°. From this amount of carbinol were obtained 126 grams of the *hydrogen phthalic* ester, which after some days in the ice chest set to a hard, crystalline mass, melting at 31—32°. It is readily resolved by the fractional crystallisation of the strychnine salt from methyl alcohol. The yield from equal quantities (12 grams) of the racemic ester and strychnine, after eight crystallisations of the salt of the pure *l*-ester, amounted to 18 grams. Further quantities of the salt were obtained from the mother liquors, twenty-one crystallisations being carried out. The *strychnine salt* of the *l*-ester melts at 129—130°, and has $[\alpha]_D$ −16·12° in chloroform. The *l*-ester, of which in all 16 grams were obtained, solidifies in rosettes of needles, which melt at 25°, and has $[\alpha]_D$ −15·60° in ethyl alcohol and $[\alpha]_D$ −11·82° in chloroform. l-*Ethyl*-n-*nonylcarbinol* is volatile in a current of steam, boils at 130°/15 mm., and sets to a hard, crystalline mass, which melts at 25°. The odour of the carbinol is very similar to that of methylnonylcarbinol (and ketone).

Ethyl-n-*decylcarbinol*, $C_{13}H_{28}O$.

A mixture of 156 grams of *n*-undecoic acid,* with 220 grams of propionic acid, passed over thoria, heated to 420°, gave 109 grams of *ethyl* n-*decyl ketone*, $C_{13}H_{26}O$,† which boils at 140°/17 mm., sets to a mass of pearly plates melting at 25°, and has only a very faint odour. In boiling *iso*amyl alcohol, it is reduced by sodium to the corresponding *carbinol* (yield, 72 per cent.), which boils at 148°/20 mm., solidifies in the ice-chest to a waxy mass of platelets, and melts at 14·5°. The racemic *hydrogen phthalic* ester is very soluble in light petroleum, melts at 46—47°, and can be resolved by the fractional crystallisation of the strychnine salt from methyl alcohol. The resolution was carried out twice, most perplexing results being obtained, as the least soluble strychnine salts separating out at different stages appeared to correspond in an erratic manner with both that of the *l*-ester and that of the *d*-ester. The resolution was then repeated a third time, care being taken to carry out each crystallisation under similar conditions as to temperature, the details of the crops being as follows: 117 grams of the racemic ester and 114 grams of strychnine were dissolved in half a litre of methyl alcohol, the crystals (crop *A*) which separated out being recrystallised six times (crops *B* to *G*), each

* Completely free from undecenoic acid.

† A second preparation gave 96 grams of the ketone from a mixture of 128 and 300 grams of respective acids.

...e from about 100 to 150 c.c. of the solvent. Crop E weighed ... grams, and melted at 131—132°; crop F, weighing 13 grams, ... identical with crop G as regards melting point (132°) and ...atory power ($[\alpha]_D$ −24·80° in chloroform), and was the pure *strychnine* salt of the *d*-ester.* The mother liquor from crop A ... concentrated, and crop B_1, amounting to 55 grams, obtained. ...rop B_1 was recrystallised from the mother liquor of crop C, the ...rystals, crop C_1, amounting to 35 grams. In a similar manner ...rops D_1, E_1, F_1 were obtained, F_1 † being then recrystallised five ...imes from fresh lots of solvent, giving crops G_1, H_1, K_1, L_1, and M_1. The crystals of crop M_1, which amounted to 9 grams, when ...eated very slowly, melted at 119—120°, had $[\alpha]_D$ −14·58° in chloroform, and consisted of the *strychnine* salt of the *l*-ester.‡ The remaining liquors were decomposed, details relating to the ...spective esters obtained from them being given in table VI.

TABLE VI.

...olution of the Hydrogen Phthalic Ester of Ethyl-n-decylcarbinol.

Weight of ester (in grams).	derived from the mother liquor of crop	Rotation $[\alpha]_D$ in chloroform.*
23·0	A	−2·6°
36·0	B_1	+0·8
13·0	C_1	−3·4
5·0	D_1	+2·6
21·0	E_1	+1·4
2·0	F_1	+3·1
3·0	G_1	−3·6
2·5	H_1	−8·1
1·0	K_1	−9·9
0·5	L_1	−11·9
0·5	M_1	−13·1

* Not specially purified. The same sample of chloroform was used for each of ... determinations recorded.

The *d*- and *l*-*esters* obtained from the corresponding pure ...trychnine salts (crop G to the *d*-ester and crop M_1 to the *l*-ester) ...olidified after evaporation of their solutions in ether to hard, ...rystalline masses, each of which melted at 35—35·5°. Deter...minations of the rotatory power gave the following results: For ...the *d*-*ester*, $[\alpha]_D$ +12·84° and +17·58°; for the *l*-*ester*, $[\alpha]_D$ −12·83° ...and −17·71°; the determinations in each case being in chloroform ...and ethyl alcohol respectively.

0·1 Gram of both esters was separately and accurately weighed ...ut, mixed, and dissolved in pure chloroform. After evaporation ...f the solvent, the resulting hard, crystalline mass melted sharply

* *S.c.*

† The mother liquor from the crop G was decomposed along with crop A to ...tain the *l*-ester.

‡ *S.c.*

at 16°, that being the melting point of the racemic ester previously obtained.* The optically active forms of *ethyl*-n-*decylcarbinol* are volatile in a current of steam, and each melts at 32°. Approximately equal amounts of each were mixed together on a porous tile, when the mixture rapidly fused, and was absorbed by the tile, the temperature of the room being 17°, and the melting point of the racemic carbinol 14·5°. The *d*-carbinol (from the *d*-ester) boiled at 139°/12 mm., and the *l*-carbinol at 140°/15 mm., each crystallising from ethyl alcohol in long and slender, silky needles.

Ethyl-n-*undecylcarbinol*, $C_{14}H_{30}O$.

Ethyl n-*undecyl ketone*, $C_{14}H_{28}O$, is readily prepared by passing a mixture of equal amounts of lauric and propionic acids over thorium oxide oxide heated to 425°, the yield being just over 60 per cent. of the lauric acid employed. It boils at 148°/10 mm., solidifies in nacreous plates, melts at 33° (compare Blaise and Guérin (*Bull. Soc. chim.*, 1903, [iii], **29**, 1208), and when dissolved in boiling amyl alcohol, is reduced by sodium to the corresponding

* Another remarkable case which in some respects is possibly analogous to the uncommon phenomenon just described has been investigated in these laboratories. Pope and Read (T., 1912, **101**, 758) have described the externally compensated and optically active hydroxyhydrindamines, recommending the latter as serviceable bases for the resolution of externally compensated acids. With the kind concurrence of Prof. W. J. Pope we have prepared and resolved a large quantity of the externally compensated hydroxyhydrindamine, following the directions given in the above-mentioned paper. However, as we had available the ammonium salt of only *d*-α-bromocamphor-π-sulphonate we expected to be able to prepare only the *l*-hydroxyhydrindamine as Pope and Read obtained the *lBdA*-salt as the least soluble component of the mixture formed by addition of an aqueous solution of ammonium *d*-α-bromocamphor-π-sulphonate (1 mol.) to an aqueous solution of *dl*-hydroxyhydrindamine hydrochloride (2 mols.). To our surprise, however, we obtained instead the *dBdA*-salt, from which was obtained the pure *d*-hydroxyhydrindamine with $[\alpha]_D$ +22·8° in water as described by Pope and Read. Our colleague, Mr. Yates, then carefully repeated the resolution, not only as described by Pope and Read, but also under varied conditions of temperature and concentration, and used throughout the ammonium salt of the dextrorotatory acid only. In each case the salt separating out was the *dBdA*-isomeride (m. p. 152°). Prof. Pope then very kindly forwarded a small specimen of the *lBdA*-salt (m. p. 224°). Following then the directions of Pope and Read, the accumulation of partially levorotatory hydroxyhydrindamine hydrochloride was (by use of the seed) converted into the *lBdA*-salt by the double decomposition of the hydrochloride and the ammonium *d*-α-bromocamphor-π-sulphonate in the required proportions calculated from the rotatory power of the hydrochloride. In this way a good yield of both the dextrorotatory and levorotatory forms of hydroxyhydrindamine was obtained from the resolution, the ammonium salt of the dextrorotatory acid only being employed. These bases appear to have no advantage over the commoner alkaloids for use in the resolution of externally compensated hydrogen phthalic or succinic esters.

ethyl-n-undecylcarbinol (yield, 80 per cent.), which boils at 173°/25 mm., solidifies in stellate masses of long needles with a pearly lustre, and melts at 25°. The *hydrogen phthalic* ester of the carbinol crystallises from light petroleum, and melts at 58—60°. The resolution of this ester by the fractional crystallisation of the strychnine salts from methyl alcohol was carried out in a manner as described for similar compounds. Thus, 158 grams of the ester and 145 grams of strychnine were dissolved in methyl alcohol, and the crop of crystals (160 grams) deposited when the solution was cooled was recrystallised six times, there being obtained 37 grams of the *strychnine* salt of pure *l*-ester, which crystallises from methyl alcohol in clear, transparent prisms, melts at 100—101°, and has $[\alpha]_D$ − 13·96° in chloroform. The mother liquors were systematically worked up as usual, the product obtained after three recrystallisations from fresh solvent having identical properties with those of the main lot (37 grams) of the pure salt. The l-*hydrogen phthalic* ester is very soluble in light petroleum, from which it crystallises in feathery needles, melts at 33°, and has $[\alpha]_D$ − 13·79° and −17·43° in chloroform and ethyl alcohol respectively. l-*Ethyl-n-undecylcarbinol* is only very slowly volatile in a current of steam, boils at 146°/10 mm. or 160°/15 mm., sets on cooling to a hard, crystalline mass, can be recrystallised from ethyl alcohol, from which it separates in stout prisms, and melts at 38°.

Ethyl-n-dodecylcarbinol, $C_{15}H_{32}O$

This carbinol was prepared by interaction of magnesium ethyl bromide and *n*-tridecaldehyde. The required aldehyde was prepared by Le Sueur's method (*loc. cit.*), but the yields were poor, as from 210 grams of pure α-hydroxymyristic acid only 62 grams of the pure aldehyde were obtained. The Grignard reaction proceeds quite smoothly, in two separate experiments the yields obtained of the carefully fractionated carbinol being 36 and 14 grams from 48 and 14 grams respectively of the aldehyde. *Ethyl-n-dodecylcarbinol* boils at 163°/12 mm., and sets on cooling to an opaque, crystalline mass, which melts at 32°. Seventy-three grams of the pure racemic *hydrogen phthalic* ester were obtained from 50 grams of the racemic carbinol. The ester crystallises from light petroleum, and melts at 54—55°. The resolution of the ester by the fractional crystallisation of the strychnine salt from methyl alcohol proceeded with unusual rapidity. Seventy-three grams of the ester and 65 grams of strychnine were dissolved in methyl alcohol (100 c.c.). After cooling, 82 grams of crystals were deposited, whilst the ester obtained from the mother liquor had $[\alpha]_D$ + 9·3° in chloroform. After three recrystallisations of

these crystals, the *strychnine* salt of the pure *l*-ester was obtained. This salt, which was unaltered by three further recrystallisations, melted at 103—104°, and had $[\alpha]_D$ −12·45° in chloroform. The *l*-ester (20 grams) obtained from the salt crystallised from light petroleum, melted at 46—47°, and had $[\alpha]_D$ −13·16° and −16·98° in chloroform and ethyl alcohol respectively. l-*Ethyl*-n-*dodecylcarbinol* is not volatile in a current of steam, boils at 168°/14 mm., sets on cooling to a hard, crystalline mass, separates from ethyl alcohol in long, silky needles, melts at 45°, and has no odour.

Ethyl n-*dodecyl ketone*, $C_{15}H_{30}O$, was prepared by the oxidation of the carbinol with chromic acid, and is slowly volatile in a current of steam. Thus purified, it is obtained in large, glistening plates, which melt at 38°.

Ethyl-n-*tridecylcarbinol*, $C_{16}H_{34}O$.

A mixture of equal amounts of myristic and propionic acids passed over thoria heated to 420° gave a 60 per cent. yield of *ethyl* n-*tridecyl ketone*, $C_{16}H_{32}O$, which boils at 184°/17 mm., and crystallises from light petroleum in lustrous leaflets, melting at 42°. When reduced by sodium in boiling *iso*amyl alcohol, it gave the corresponding *carbinol*, which boils at 176°/16 mm., and on cooling sets to a hard, crystalline mass, melting at 37—38°. The *hydrogen phthalic* ester separates from light petroleum in clusters of silky needles, and melts at 51—52°.

The resolution of the ester was carried out in the usual manner by the fractional crystallisation of the strychnine salt from acetone containing a small amount of chloroform. A mixture of the ester (126 grams) and strychnine (108 grams) was dissolved in chloroform, which was then removed as completely as possible by distillation on a water-bath, the resulting paste being quickly dissolved in warm acetone. The crystals deposited from this solution weighed 67 grams, and were recrystallised six times in a similar manner, 27 grams of the strychnine salt of the pure *l*-ester being obtained. After recrystallisation of the products given by systematically working up the mother liquors, a further quantity of the pure salt was obtained, the *l*-ester from both lots of salt amounting to 26 grams. The *strychnine* salt of the *l*-ester crystallises from acetone in stout, glassy rods, melts at 103—104° and has $[\alpha]_D$ −11·66° in pure chloroform. The *l*-ester crystallises from light petroleum in prismatic needles, melts at 51°, and has $[\alpha]_D$ −12·55° and −16·47° in pure chloroform and ethyl alcohol respectively. l-*Ethyl*-n-*tridecylcarbinol* is not readily volatile in a current of steam, it boils at 152°/4 mm., melts at 50°, separates

from ethyl alcohol in rosettes of very slender needles, and is almost odourless.

Ethyl-n-*pentadecylcarbinol*, $C_{18}H_{38}O$.

A warm solution of palmitic acid (300 grams) in propionic acid (100 grams) was passed over thoria heated to 430°, and 114 grams of *ethyl* n-*pentadecyl ketone*, $C_{18}H_{36}O$, were obtained, 102 grams of pure palmitic acid being recovered. The ketone boils at 198°/14 mm., and sets on cooling to a crystalline mass, melting at 50°. When reduced in boiling *iso*amyl alcohol by means of sodium, the corresponding *carbinol* is formed, the yield being 70 per cent. This boils at 202°/13 mm., and melts at 43°. The *hydrogen phthalic ester*, as prepared in the usual manner, melted at 39—41°, but was probably not quite pure, as the solutions of the sodium salt are of a soapy character and difficult to extract with ether. The resolution of the ester was carried out by an analogous method to those described above. The ester (118 grams) and strychnine (80 grams) were dissolved in methyl alcohol, the solution concentrated, and allowed to remain in the ice-chest. The crop of crystals obtained melted at 84—87°, and was recrystallised six times from methyl alcohol, the final crop weighing 30 grams, and melting at 108—109°. The *strychnine* salt of the *l*-ester had $[\alpha]_D$ −12·57° in chloroform, a further quantity being obtained from a systematic working up of the mother liquors (five operations), and recrystallising the product three times from fresh solvent. From both lots of the salt 19·5 grams of the l-*ester* were obtained; it melts at 32—33°, and has $[\alpha]_D$ −15·62° and −12·16° in ethyl alcohol and chloroform respectively. l-*Ethyl*-n-*pentadecylcarbinol* boils at 172°/2 mm., melts at 56°, separates from ethyl alcohol in small, prismatic rods, and is odourless.

Density Determinations.

The following density determinations were carried out in a pyknometer holding 4 c.c., and are compared with water at 4°:

l-*Ethyl*-n-*propylcarbinol*: at 13·5°, 0·8246; at 53·5°, 0·7916; at 84°, 0·7627; at 104°, 0·7428.

d-*Ethyl*-n-*butylcarbinol*: at 13°, 0·8248; at 50°, 0·7985; at 88°, 0·7603; at 127°, 0·7245.

d-*Ethyl*-n-*amylcarbinol*: at 19°, 0·8231; at 48°, 0·8016; at 89°, 0·7648; at 125°, 0·7302.

d-*Ethyl*-n-*hexylcarbinol* (as given in Part I), and at 124°, 0·7489.

l-*Ethyl*-n-*heptylcarbinol*: at 12·5°, 0·8310; at 48°, 0·8071; at 90°, 0·7715; at 137°, 0·7330.

l-*Ethyl*-n-*octylcarbinol*: at 17°, 0·8308; at 50°, 0·8076; at 81°, 0·7823; at 128°, 0·7426.

l-*Ethyl*-n-*nonylcarbinol*: at 32°, 0·8223; at 61°, 0·7999; at 91°, 0·7748; at 124°, 0·7467.

d-*Ethyl*-n-*decylcarbinol*: at 46°, 0·8139; at 69°, 0·7965; at 93°, 0·7755; at 128°, 0·7466.

l-*Ethyl*-n-*decylcarbinol*: at 43°, 0·8180; at 80°, 0·7889.

l-*Ethyl*-n-*undecylcarbinol*: at 53°, 0·8098; at 78°, 0·7896; at 98°, 0·7748; at 146·5°, 0·7354.

l-*Ethyl*-n-*dodecylcarbinol*: at 55°, 0·8115; at 82°, 0·7908; at 94°, 0·7816; at 132°, 0·7518.

l-*Ethyl*-n-*tridecylcarbinol*: at 67°, 0·8000; at 90°, 0·7843; at 119°, 0·7611; at 153°, 0·7335.

l-*Ethyl*-n-*pentadecylcarbinol*: at 73°, 0·8011; at 90°, 0·7876; at 121°, 0·7618.

Determination of the Rotatory Powers of the Carbinols in the Homogeneous State.

The determinations of the rotatory powers of the carbinols in the homogeneous state have been made in jacketed tubes, 50 mm. and 100 mm. in length, round which a heated mineral oil was circulated by a pump. The temperature was carefully observed by a standardised thermometer placed in the liquid under observation, and the general practice was to make a series of readings with (say) the yellow sodium light whilst the temperature was rising, and another series with the green mercury light whilst it was falling. In each case similar curves were obtained for both wave-lengths, and no evidence was obtained that any racemisation had ensued during the heating. The figures given below are either those obtained from observations in a 100 mm. tube or have been calculated for that length:

*l-*Ethylpropylcarbinol*: α_D at 22·5°, −1·62°; at 58°, −1·64°; at 87°, −1·68°; and at 108°, −1·72°.

α_{5461} at 22·5°, −1·84°; at 73°, −1·90°; at 102°, −1·94°; and at 117°, −1·96°.

d-*Ethyl*-n-*butylcarbinol*: α_D at 20·5°, +6·68°; at 54°, +6·54°; at 57°, +6·52°; at 70°, +6·46°; at 104°, +6·34°; and at 130°, +6·21°.

α_{5461} at 20·5°, +7·88°; at 77°, +7·54°; at 97°, +7·46°; at 105°, +7·40°; at 120°, +7·34°; and at 134°, +7·26°.

d-*Ethyl*-n-*amylcarbinol*: α_D at 18°, +6·79°; at 23°, +6·76°; at 55°, +6·69°; at 63°, +6·60°; at 94°, +6·46°; at 111°, +6·38°; at 130°, +6·28°; and at 160°, +6·05°.

α_{5461} at 23°, +7·91°; at 42°, +7·86°; at 52°, +7·80°; at 63°,

* *Methylethylcarbinol* (see p. 1941).

+7·76°; at 82°, +7·66°; at 93°, +7·62°; at 108°, +7·48°; at 120°, +7·36°; at 133°, +7·30°; and at 145°, +7·20°.

l-*Ethyl-n-hexylcarbinol:* α_D at 19°, −6·10°; at 48°, −6·12°; at 56°, −6·14°; at 62°, −6·12°; at 70°, −6·10°; at 87°, −6·00°; at 111°, −5·86°; at 128°, −5·74°; and at 152°, −5·52°.

α, at 19°, −7·12°; at 45°, −7·16°; at 52°, −7·14°; at 64°, −7·06°; at 80°, −7·00°; at 101°, −6·90°; at 112°, −6·84°; at 131°, −6·66°; and at 149°, −6·50°.

l-*Ethyl-n-heptylcarbinol:* α_D at 21°, −5·54°; at 47°, −5·42°; at 72°, −5·33°; at 92°, −5·19°; at 100°, −5·14°; at 132°, −4·90°; and at 148°, −4·78°.

α, at 19·5°, −6·42°; at 63°, −6·20°; at 68°, −6·16°; at 73°, −6·12°; at 91°, −6·100°; at 96°, −5·96°; at 112°, −5·86°; at 135°, −5·64°; and at 142·5°, −5·60°.

l-*Ethyl-n-octylcarbinol:* α_D at 22°, −5·21°; at 38°, −5·17°; at 58°, −5·12°; at 86°, −4·98°; at 100°, −4·90°; at 132°, −4·72°; and at 145°, −4·64°.

α, at 20·5°, −6·02°; at 43°, −5·96°; at 76°, −5·80°; at 95°, −5·70°; at 116°, −5·56°; at 128°, −5·54°; and at 157°, −5·28°.

l-*Ethyl-n-nonylcarbinol:* α_D at 29·5°, −4·80°; at 31°, −4·76°; at 36°, −4·68°; at 62°, −4·44°; at 70°, −4·38°; at 85°, −4·32°; at 100°, −4·24°; at 122°, −4·12°; at 135°, −4·10°; and at 157°, −4·06°.

α, at 30°, −5·54°; at 51·5°, −5·20°; at 76°, −5·00°; at 90°, −4·90°; at 112°, −4·80°; at 137°, −4·68°; and at 152°, −4·64°.

d-*Ethyl-n-decylcarbinol:* α_D at 12°, +5·04°; at 63°, +4·90°; at 92°, +4·72°; at 107°, +4·64°; at 120°, +4·56°; at 131°, +4·50°; and at 158°, +4·38°.

α, at 38°, +5·90°; at 68°, +5·66°; at 83°, +5·54°; at 102°, +5·40°; at 127°, +5·20°; at 150° +5·08°; and at 168°, +5·02°.

l-*Ethyl-n-decylcarbinol:* α_D at 76°, −4·82°.

l-*Ethyl-n-undecylcarbinol:* α_D at 42°, −4·74°; at 53°, −4·64°; at 79°, −4·52°; at 85°, −4·46°; at 105°, −4·40°; at 117°, −4·31°; at 138°, −4·18°; and at 166°, −4·02°.

α, at 41°, −5·49°; at 47·5°, −5·46°; at 53°, −5·40°; at 70°, −5·29°; at 90°, −5·19°; at 113°, −5·08°; at 119°, −5·01°; at 133°, −4·94°; and at 141°, −4·87°.

l-*Ethyl-n-dodecylcarbinol:* α_D at 53°, −4·40°; at 61°, −4·32°; at 84°, −4·20°; at 104°, −4·12°; at 134°, −4·02°; and at 158°, −3·92°.

α, at 16°, −5·14°; at 68°, −4·96°; at 75°, −4·92°; at 86° −4·86°; at 99°, −4·78°; at 116°, −4·72°; at 130°, −4·64°; at 140°, −4·62°; and at 155°, −4·60°.

l-*Ethyl*-n-*tridecylcarbinol*: α_D at 50°, −4·14°; at 57°, −4·12°; at 90°, −3·94°; at 114°, −3·78°; and at 148°, −3·58°.

α_{gr} at 58°, −4·78°; at 78°, −4·66°; at 98°, −4·50°; at 125°, −4·30°; and at 149°, −4·14°.

l-*Ethyl*-n-*pentadecylcarbinol*: α_D at 64°, −3·84°; at 77°, −3·78°; at 102°, −3·64°; at 120°, −3·58°; at 141°, −3·50°; and at 151°, −3·40°.

α_{gr} at 61°, −4·44°; at 67°, −4·42°; at 71°, −4·40°; at 96°, −4·30°; at 113°, −4·20°; at 118°, −4·16°; at 136°, −4·10°; and at 161°, −3·80°.

For the purpose of testing whether the optical rotatory dispersion Na_{yellow}/Hg_{green} is constant over the available range of temperature, new preparations of methyl-*n*-butyl-, -*n*-hexyl-, and -*n*-nonyl-carbinols, as well as of *n*-propyl*iso*propylcarbinol and *iso*propyl-*n*-hexylcarbinol have been examined. The following polarimetric observations agree well with those recorded in Parts I and II.

d-*Methyl*-n-*butylcarbinol*: α_D at 20°, +9·08°; at 42°, +8·60°; at 64°, +8·19°; at 80°, +8·00°; at 96°, +7·83°; at 110°, −7·73°; and at 119°, −7·62°.

α_{gr} at 21°, +10·82°; at 43°, +10·06°; at 56°, +9·79°; at 70°, +9·49°; at 80°, +9·33°; at 95°, −9·13°; at 105°, +9·07°; and at 123°, +8·95°.

The values of the optical dispersive power calculated from the smoothed curves from these figures are: at 20°, 0·844; at 40°, 0·848; at 60°, 0·848; at 80°, 0·851; at 100°, 0·851; and at 120°, 0·848, the mean value being 0·848. This alcohol has been prepared recently in larger quantities, but the authors have not been able to prepare material with $[M]_D$ at the boiling point so high as that (11·3°) given in Part I, the value $[M]_D$ 10·9° being the highest obtained lately.

d-*Methyl*-n-*hexylcarbinol*: α_D at 20°, +8·05°; at 48°, +7·51°; at 54°, +7·38°; at 70°, −7·13°; at 101°, +6·76°; at 110°, +6·68°; and at 142°, +6·35°.

α_{gr} at 19°, +9·61°; at 48°, +8·90°; at 62°, −8·55°; at 74°, −8·36°; at 95°, +8·07°; at 120°, +7·80°; and at 139·5°, +7·63°. The values of the dispersive power calculated from these observations are: at 20°, 0·845; at 40°, 0·845; at 60°, 0·847; at 80°, 0·845; at 100°, 0·845; at 120°, 0·844; and at 140°, 0·842, the average value being 0·845.

d-*Methyl*-n-*nonylcarbinol*: α_D at 142°, +5·24°.

α_{gr} at 23°, +7·85°; at 45°, +7·28°; at 57°, +7·01°; at 76°, −6·78°; at 95°, +6·56°; at 113°, +6·45°; at 135°, +6·23°; and at 151°, +6·12°.

From these and previously recorded (Part I) observations, the calculated values of the optical dispersive power are: at 20°, 0·849; at 40°, 0·849; at 60°, 0·854; at 80°, 0·854; at 100°, 0·847; at 120°, 0·844; and at 140°, 0·845, the average value being 0·849.

*d-Propyl-*iso*propylcarbinol:* α_D at 19°, +17·66°; at 31°, +17·48°; at 45°, +17·18°; and at 98°, +15·54°.

α at 19°, +20·94°; at 30°, +20·64°; at 40°, +20·40°; at 55°, +20·08°; at 65°, +19·74°; at 98°, +18·38°; at 111°, +17·88°; at 116·5°, +17·46°; and at 121°, +17·22°. These observations, with others previously recorded, give the following values of the optical rotatory dispersive power: at 20°, 0·844; at 40°, 0·844; at 60°, 0·842; at 80°, 0·840; at 100°, 0·843; at 120°, 0·843; and at 140°, 0·842, the average value being 0·843.

*iso*Propyl-d-*hexylcarbinol:* α_D at 18·5°, +17·86°.

α at 18·5°, +21·24°; at 40°, +20·60°; at 62°, +19·94°; at [illegible], +18·46°; at 112°, +17·96°; at 127°, +17·42°; and at 147°, +16·50°. The values of the optical rotatory dispersive power calculated from these and previously recorded observations are: at 20°, 0·841; at 40°, 0·842; at 60°, 0·840; at 80°, 0·839; at 100°, 0·840; at 120°, 0·840; at 140°, 0·840; and at 160°, 0·841, the average value being 0·840.

Determinations of the Rotatory Power in Absolute Ethyl Alcohol.

Carbinols, $CH_3 \cdot CH(OH) \cdot R$.

	Weight taken in grams.	Observed rotation. α_D	$[\alpha]_D$	$[M]_D$
Methylethylcarbinol	1·0167	+1·48°	14·55°	+10·77°
Methyl-*n*-propylcarbinol	1·0641	1·65	15·51	13·65
Methyl-*n*-butylcarbinol	1·0471	1·33	12·70	12·95
Methyl-*n*-amylcarbinol	1·0392	1·19	11·45	13·28
Methyl-*n*-hexylcarbinol	1·0923	1·07	9·79	12·73
Methyl-*n*-heptylcarbinol	1·1427	1·04	9·10	13·10
Methyl-*n*-octylcarbinol	1·0126	0·90	8·89	14·04
Methyl-*n*-nonylcarbinol	1·0229	0·83	8·11	13·95
Methyl-*n*-decylcarbinol	0·8694	0·69	7·94	14·76
Methyl-*n*-undecylcarbinol	1·0174	0·75	7·37	14·71

Carbinols, $CH(CH_3)_2 \cdot CH(OH) \cdot R$.

*iso*Propylmethylcarbinol	0·9555	+0·52	5·44	+4·79
*iso*Propylethylcarbinol	1·0670	1·75	16·40	16·73
*iso*Propyl-*n*-propylcarbinol	0·9942	2·32	23·34	27·07
*iso*Propyl-*n*-butylcarbinol	1·0589	2·93	27·67	35·97
*iso*Propyl-*n*-amylcarbinol	0·9713	2·58	26·56	38·24
*iso*Propyl-*n*-hexylcarbinol	1·1242	2·73	24·28	38·36
*iso*Propyl-*n*-octylcarbinol	1·0002	2·15	21·50	39·99
*iso*Propyl-*n*-decylcarbinol	1·1852	2·18	18·34	39·38

Determinations of the Rotatory Power in Absolute Ethyl Alcohol (continued).

Carbinols, $C_2H_5{\cdot}CH(OH){\cdot}R$.

	Weight taken in grams.	Observed rotation, α_D.	$[\alpha]_D$	$[M]_D$
Ethyl-*n*-propylcarbinol	1·0426	−0·12°	1·15°	1·17
Ethyl-*n*-butylcarbinol	1·0070	+0·97	9·63	11·17
Ethyl-*n*-amylcarbinol	0·9791	+1·09	11·13	14·47
Ethyl-*n*-hexylcarbinol...........	1·0182	+0·98	9·63	13·86
Ethyl-*n*-heptylcarbinol	0·9995	0·62	6·21	9·81
Ethyl-*n*-octylcarbinol	1·0449	−0·65	6·22	10·69
Ethyl-*n*-nonylcarbinol	1·1144	−0·68	6·10	11·35
Ethyl-*n*-decylcarbinol.......... ..	0·9510	−0·64	6·73	13·46
Ethyl-*n*-undecylcarbinol.........	1·0728	−0·67	6·25	13·38
Ethyl-*n*-dodecylcarbinol.........	1·0988	−0·60	5·46	12·44
Ethyl-*n*-tridecylcarbinol	1·0461	−0·55	5·27	12·75
Ethyl-*n*-pentadecylcarbinol ...	1·0047	−0·48	4·78	12·91

Determination of Rotatory Power of Carbinols, $C_2H_5{\cdot}CH(OH){\cdot}R$, *in Benzene.*

Dextrorotatory Carbinols, $CH_3{\cdot}CH(OH){\cdot}R$.

Methyl-*n*-propylcarbinol ...	0·8059	+1·41°	+17·87°	+15·7[illegible]
Methyl-*n*-butylcarbinol	1·0112	1·41	13·95	14·23
Methyl-*n*-amylcarbinol	0·9918	1·36	13·71	15·90
Methyl-*n*-hexylcarbinol	1·1011	1·37	12·44	16·77
Methyl-*n*-heptylcarbinol ...	1·0000	1·19	11·90	16·98
Methyl-*n*-octylcarbinol	0·9953	1·14	11·46	18·10
Methyl-*n*-nonylcarbinol ...	1·0303	1·06	10·29	17·69
Methyl-*n*-decylcarbinol	0·6808	0·68	9·99	18·57
Methyl-*n*-undecylcarbinol ...	1·0150	0·89	8·74	17·48

	Weight taken in grams.	Observed rotation α_D	$[\alpha]_D$	$[M]_D$	Observed rotation α	$[\alpha]$	$[M]$
d-Ethyl-methylcarbinol	1·0632	+1·50	+14·11	+10·44°	+1·71°	+16·09	+11·9
l-Ethyl-*n*-propylcarbinol...	1·0356	−0·19	−1·83	−1·87	−0·28	−2·70	−2·7[illegible]
d-Ethyl-*n*-butylcarbinol ...	1·0092	+0·94	+9·31	+10·80	+1·08	+10·70	+12·41
d-Ethyl-*n*-amylcarbinol	1·0196	+1·04	+10·20	+13·36	+1·16	+11·38	+14·79
d-Ethyl-*n*-hexylcarbinol	1·0417	+1·00	+9·60	+13·82	+1·13	+10·85	+15·62
l-Ethyl-*n*-heptylcarbinol ...	1·0434	0·80	−7·67	−12·11	−0·94	9·01	14·24
l-Ethyl-*n*-octylcarbinol	0·9886	0·70	7·08	12·18	−0·86	8·70	−14·96
l-Ethyl-*n*-nonylcarbinol ..	1·0737	0·72	−6·71	−12·48	−0·89	−8·29	−15·41
l-Ethyl-*n*-decylcarbinol	0·9581	0·70	−7·31	14·62	−0·80	−8·35	−16·70
l-Ethyl-*n*-undecylcarbinol.	1·0282	0·75	7·29	−15·60	−0·88	8·56	−18·32
l-Ethyl-*n*-dodecylcarbinol.	0·9522	0·64	−6·72	−15·32	−0·76	−7·98	18·20
l-Ethyl-*n*-tridecylcarbinol.	1·0659	0·68	−6·38	−15·44	−0·83	−7·79	−18·85
l-Ethyl-*n*-pentadecylcarbinol.	1·0067	−0·62	−6·16	−16·63	−0·75	−7·45	−20·12

The authors have much pleasure in acknowledging the able assistance given to them by Mr. William Osbaldiston, who has prepared much of the material for this research, and by Mr. John Ranson, who helped during its later stages; and further, desire to express their thanks to the Government Grant Committee of the Royal Society for grants which have defrayed some of the expense of this investigation.

MUNICIPAL TECHNICAL SCHOOL,
BLACKBURN.

CCVIII.—*The Rate of Hydration of Acid Anhydrides: Acetic, Propionic, Butyric, and Benzoic.*

By BERNARD HOWELL WILSDON and NEVIL VINCENT SIDGWICK.

THE method adopted in this work is essentially that described by Rivett and Sidgwick (T., 1910, **97**, 732, 1677). The rate of formation of the acid is determined by measuring the increase of the electrical conductivity of a solution of the anhydride in water. For this purpose it was necessary to know the conductivities of the acids investigated, up to the concentration obtained from a saturated solution of the anhydride. The viscosities were also measured, and an allowance was made for this on the assumption that Stokes' law holds for ions in solution, and hence that the ionic mobilities are inversely proportional to the viscosity.

I.—*Conductivity, Density, and Viscosity.*

Two cells were used, one having large vertical electrodes covered with grey platinum, and the other smaller horizontal plates coated with platinum black. It was originally intended to have grey platinum in the second cell also, but with the smaller electrodes the "minimum" was found to be so bad in the stronger solutions as to introduce an error larger than any likely to result from adsorption by the platinum black. A Wheatstone-Kirchhoff roller bridge was used,* together with a Nernst induction coil

* It does not seem to be generally recognised, although it is obvious enough when once it is pointed out, that in conductivity measurements under the ordinary conditions of experiment, the sensitiveness of a Wheatstone bridge is practically proportional to the resistance of the bridge wire. The change of sound in the telephone for a displacement of the sliding contact by, say, 0·1 mm. with a metre bridge, will be proportional to the fall of potential over 0·1 mm. of the wire, and therefore to the difference of potential between the ends of the [illegible]

The dilutions were made in the cell, which was first partly filled with conductivity water, and then a solution of the acid of known strength added from a weight pipette. In all cases several series of measurements were made with different original solutions. The water was obtained from a Hartley still, and its conductivity at 25° was from 0·8 to 1·5 gemmhos.

At the dilute end of the conductivity curve, the water correction becomes very considerable. The error may be avoided in measuring the velocity of hydration, if we use water of the same quality for the velocity experiments; but if we are to determine the value of the dissociation constant, it is necessary to know how the correction is to be applied. Our results indicate that fairly constant values of the Ostwald dissociation constant are obtained, even at dilutions where the correction is a large fraction of the total conductivity, when the conductivity of the water is added to that of the solution. At extreme dilution, however, the values thus obtained are too high. The theoretical justification for adding the correction is not easy to understand. If the conductivity of the water is mainly due to hydrogen ion, a negative correction would be required. If it is due either to sodium hydroxide from the glass, to ammonia, or to ammonium carbonate, some positive correction is necessary. A further positive correction is probably required at the higher dilutions, owing to adsorption by the plates. The method of simply adding the conductivity of the water seems, judging by the results, to give approximately the correction required.

The densities of the solutions were determined with pyknometers of test-tube glass, of about 25 c.c. capacity, and the viscosities with Ostwald viscometers, the water values of which were four to five minutes.

In the following tables* are given (1) the volume normality, (2) the specific conductivity uncorrected for water, (3) the molecular conductivity μ, and (4) the dissociation constant K, corrected by adding the conductivity of the water, and further by multiplying by the viscosity.

resistance of the bridge wire, however, is small in comparison with that of the whole circuit—including the secondary coil of the inductorium—of which it forms a part. Hence the fall of potential between the ends of the bridge, and therefore its sensitiveness, vary very nearly with the resistance of the bridge wire.

* In Tables I—V only a portion of those measurements which were used in obtaining a mean value of K are quoted.

1.—*Acetic Acid.*

Kahlbaum's purest acid, which had been frozen out and drained off from the liquid, was used. μ_a was taken as 353·0.

Table I.

Conductivity of Acetic Acid at 18°.*

Vol. norm.	Sp. cond.	Mol. cond.	$K \times 10^7$.
0·002807	0·07597	27·13	179·6
0·004462	0·09590	21·78	181·0
0·007703	0·12700	16·66	179·0
0·02246	0·2187	9·813	178·5
0·03470	0·2722	7·902	177·8
0·07273	0·3910	5·435	175·2
0·1702	0·5990	3·595	177·8
0·4180	0·9462	2·224	178·9
0·8118	1·211	1·639	175·9
1·599	1·504	—	—
2·939	1·638	—	—
4·143	1·576	—	—

* The values for acetic acid at 25° are given by Rivett and Sidgwick, *loc. cit.*, p. 731–736.

*Viscosity and Density.**

Vol. norm.	Density.	Viscosity.
5·0658	1·0128	1·7912
1·9891	1·0163	1·2366

* Throughout this paper the densities and viscosities are referred to water at the same temperature as unity.

Three series of measurements were made. In the first and second the conductivity of the water was 1·01 gemmhos; in the third, 1·23 gemmhos.

The mean of 16 values of K, from 182·0 to 175·2, is 178·8. The maximum divergence from the mean is 2·0 per cent. It will be seen from the table that the greatest differences occur at the beginning of each series, where any error arising from differences in absorption at the electrodes of the two cells used will have the maximum effect.

By using this value for the dissociation constant of acetic acid, together with that (re-calculated) obtained by Rivett and Sidgwick, we can calculate the heat of ionisation Q for the temperature interval 18–25°:

$$K_{25} = 187·9$$
$$K_{18} = 178·8$$
$$\log_e \frac{187·9}{178·8} = -\frac{Q}{R}\left(\frac{1}{291} - \frac{1}{298}\right).$$
$$Q = -1·3421 \text{ kg. Cal.}$$

Lundén gives for temperatures from 10° upwards the value $-0.675+0.0315$ kg. Cal., but there is such divergence between the values of different observers, obtained by different methods, that it is impossible to judge of the correctness of this result.

2.—*Propionic Acid.*

Kahlbaum's purest acid was distilled twice, and the fraction boiling at 140·9–141·0° (uncorr.) was used; μ_∞ was taken as 401·6 at 25°, and 319·0 at 18°.

TABLE II.

Conductivity of Propionic Acid at 25°.

Vol. norm.	Sp. cond.	Mol. cond.	$K \times 10^7$.
0·006776	0·1120	16·56	122·1
0·01415	0·1646	11·43	121·6
0·02581	0·2217	8·634	123·3
0·04862	0·3031	6·297	122·2
0·08097	0·3906	4·901	122·7
0·1469	0·5221	3·659	123·5
0·3649	0·7577	2·309	121·7
0·8990	1·027	–	[112·4]
1·673	1·131	–	[107·5]

In one of the two series, conductivity of water was 0·73 gemmhos; in the other, 1·20 gemmhos.

Viscosity and Density at 25°.

Vol. norm.	Density.	Viscosity.
1·817	(1·0197)	1·3542
1·379	1·0081	1·2668
0·9893	(1·0059)	1·1877
0·6496	(1·0039)	1·1244
0·4457	1·0026	1·0862
0·2594	1·0023	1·0500

Values in brackets were interpolated from the curve.

The values of K are not given below 0·36 normal, as at this point they begin to fall regularly. The mean of 21 values, ranging from 121·4 to 123·5, gives K as 122·5, with a maximum error of 0·9 per cent.

TABLE III.

Conductivity of Propionic Acid at 18°.

Vol. norm.	Sp. cond.	Mol. cond.	$K \times 10^7$.
0·001164	0·04094	35·17	135·7
0·003167	0·06884	21·75	134·4
0·006223	0·09819	15·79	135·2
0·01784	0·1674	9·416	134·8
0·02613	0·2056	7·917	137·6
0·03500	0·2347	6·751	134·5
0·04510	0·2695	6·032	137·1
0·05936	0·3085	5·259	136·9
0·09609	0·3866	4·099	134·7
0·1715	0·5091	3·069	134·2
0·3215	0·6794	—	134·0]
0·6564	0·9858	—	127·6]
0·9284	0·9942	—	122·0]

In the first two of the three series, conductivity of water was 0·70 gemmhos; in the third, 1·00 gemmhos.

The molecular conductivity at infinite dilution was taken as 349·0.

The mean of 31 values of K, ranging from 137·8 to 134·2, is 134·8, with a maximum error of 1·5 per cent.

Viscosity and Density at 18°.

Vol. norm.	Density.	Viscosity.
1·817	(1·0107)	1·3861
1·370	1·0081	1·2786
0·9825	1·0059	1·1958
0·6496	1·0039	1·1241
0·4457	1·0031	1·0852
0·2594	1·0018	1·0503

Taking the values $K_{25} \times 10^7 = 122·5$, and $K_{18} \times 10^7 = 135·8$, we get the heat of ionisation, $Q = +2·529$ kg. Cal. Arrhenius gives $Q = +0·183$ kg. Cal.

3.—*Butyric Acid (normal).*

Kahlbaum's purest acid was redistilled, and the fraction boiling at 163—163·5° (uncorr.) was used; μ_α was taken as 397·7 at 25°, the only temperature at which experiments were made.

TABLE IV.

Conductivity of Butyric Acid at 25°.

Vol. norm.	Sp. cond.	Mol. cond.	$K \times 10^5$.
0·001026	0·04372	42·61	139·1
0·001875	0·06047	32·25	139·3
0·003115	0·08290	24·28	139·5
0·005002	0·1012	20·23	139·7
0·007417	0·1239	16·71	139·4
0·01411	0·1718	12·17	139·8
0·02467	0·2271	9·203	138·8
0·04987	0·3240	6·497	140·0
0·1003	0·4547	4·645	139·4
0·19158	0·6122	—	137·6]
0·2328	0·6659	—	136·0]

Two series: conductivity of water 1·56 and 1·20 gemmhos respectively.

Viscosity and Density.

Vol. norm.	Density.*	Viscosity.
0·4771	1·00176	1·1231
0·2696	1·00100	1·0675
0·06210	1·00024	1·0156

* The values for the density are taken from Lüdeking (*Jahresber.*, 1886, 216.

Mean of 17 values of K, from 141·3 to 138·8, is 139·7. Maximum error, 1·0 per cent.

II.—*Rate of Hydration of Anhydrides.*

These measurements were carried out in the cells previously used for the conductivities. With the liquid anhydrides, a measured volume was added to the required volume of water, already warmed in the thermostat, and then the whole shaken violently for a short time, and poured into the cell. The benzoic anhydride, being solid, was finely powdered, shaken with water, and the liquid was sucked through a glass-wool filter into the cell.

The conductivity of the solution was measured from time to time, and the amount of acid present determined by interpolation on the conductivity curves. As before, the results were corrected for viscosity, on the assumptions (*a*) that the ionic velocity is inversely proportional to the viscosity, and (*b*) that the viscosity of a solution of an anhydride is equal to that of an equivalent solution of the corresponding acid. The latter has been shown to be approximately true for acetic anhydride.

The results are calculated on the unimolecular formula.

1.—*Acetic Anhydride.*

The material was Kahlbaum's anhydride "free from homologous anhydrides."

In the following table, the first column gives the (volume) normality of the acid at the end of the experiment; the second, the initial equivalent normality of the anhydride at the time, which was taken as $=0$ for calculating the velocity. The values of K are in each case the mean of more than twenty observations. The expression K' in the last column is explained below.

Table VI.

Hydration of Acetic Anhydride at 18°.

Final norm. of acid.	Initial norm. of anhydride.	K.	$K' = K \times \eta^2/C_w$.
0·00648	0·00543	0·000762	0·000763
0·00978	0·00821	742	744
0·03336	0·02655	759	765
0·05152	0·04064	737	746
0·1054	0·08513	716	735
0·1743	0·1231	739	772
0·1856	0·1490	745	784
0·1959	0·1452	741	783
0·2602	0·2096	723	779
0·2840	0·2155	729	789
0·2948	0·2436	735	800
0·3509	0·2913	718	794
0·6778	0·4875	663	806
0·7109	0·5262	649	794
1·2011	1·0349	591	823
2·2050	1·9710	459	828

For the sake of comparison, the results obtained by Rivett and Sidgwick at 25° are given in table VII, with the corresponding corrections. The first column gives the normality, the second the observed velocity constant K, and the third the corrected $K' = K \times \eta^2/C_w$.

Table VII.*

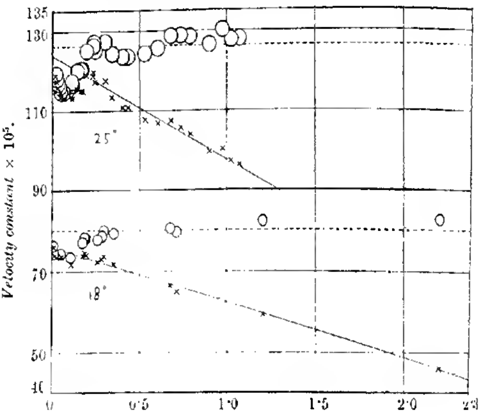
Hydration of Acetic Anhydride at 25°.

Normality.	K.	$K' = K \times \eta^2/C_w$.	Normality.	K.	$K' = K \times \eta^2/C_w$.
0·02015	0·001186	0·001192	0·4910	0·001105	0·001233
0·03307	1157	1168	0·4355	1103	1233
0·04883	1133	1146	0·5300	1075	1240
0·07575	1137	1158	0·6040	1067	1253
0·1160	1131	1164	0·6785	1072	1284
0·1670	1148	1202	0·7345	1056	1285
0·1949	1186	1249	0·7895	1059	1281
0·2339	1184	1261	0·8995	994	1261
0·2348	1192	1270	0·9745	1002	1298
0·2449	1169	1249	1·0255	971	1274
0·3028	1173	1271	1·0705	961	1276
0·3425	1130	1240			

* Some of the earlier values are omitted in this table, but they are given in the diagram.

The results are plotted in the diagram against the final concen tration of the acid; and for comparison, those obtained at 25 (R. and S.) are added. The crosses indicate the observed value ($K \times 10^5$); the circles, the values corrected as described below ($K \times \eta^2/C_w \times 10^5$); the radius of the circle corresponds to an error of 1·5 per cent. They show two peculiar phenomena: first, an irregularity at the dilute end, consisting of a fall as the concentration increases from its lowest value to about $N/10$, followed by a rise from $N/10$ to about $N/5$; and secondly, a steady fall with increase of concentration from $N/5$ upwards.

The second phenomenon may be considered first. This has the



Final normality.

same value—about 23 per cent. for an increase from $N/5$ to 1·2N—at 18° and 25°. It is confirmed by the work of Orton and Jones (T., 1912, **101**, 1709), who measured the velocity of this reaction by a wholly different method, and with a much greater concentration of acid. One influence which would cause a fall in the velocity constant is the fall in the concentration of the water as the amount of acid increases. This, however, can be allowed for. The real reaction is, of course, bimolecular:

$$Ac_2O + H_2O = 2Ac{\cdot}OH.$$

It can only be treated as unimolecular if the concentration of the water is taken as constant, which is not strictly the case, except at extreme dilution. We can, however, assume that this remains sensibly constant during an experiment; that is, that the change

n concentration due to the water taken up in the reaction is negligible, since this does not exceed 2 per cent., even when the initial (equivalent) concentration of the anhydride is normal. We re therefore justified in calculating on the unimolecular formula, ut the values obtained must be divided by the concentration of he water in each experiment (that in pure water being taken as nity) to give the true velocity constant.

This correction, however, is far from sufficient to account for the bserved fall; in fact, it only amounts to about 6 per cent. for an ncrease of $1N$, whilst the fall is some four times as great. Another actor which may explain the fall is the increase in the viscosity f the medium. If we suppose that the mobilities of the two eacting molecular species are inversely proportional to the viscosity, then the observed values ought to be multiplied by the quare of the viscosity, in order to give the intrinsic velocity onstant.

This conclusion may be expressed as follows: If the rate of eaction is proportional to the product of the concentrations of the wo reacting substances, divided by the viscosity of the solution, we have:

$$\frac{dx}{dt} = K' \times \frac{C_{\text{anh.}}}{\eta} \times \frac{C_w}{\eta}.$$

Assuming that C_w and η remain constant during an experiment, this gives on integration:

$$\frac{1}{t}\log\frac{A}{A-x} = \frac{K' \times C_w}{\eta^2},$$

where A is the initial concentration of the anhydride, and x its oncentration at time t.

The figures given in the last column of the table represent the values of the observed velocity constants corrected in this way for the concentration of the water, and for the viscosity of the medium.

It will be seen that the values of K' (from about 0·18 normal upwards) show a fair approximation to constancy, especially considering that the correction in the strongest solution is upwards of 80 per cent. The mean of all the results above 0·2 normal is 0·001263 at 25° and 0·0008017 at 18°; these are represented by the dotted horizontal lines on the diagram, and are in both cases a little higher than the values for infinite dilution obtained by drawing a straight line through the values of K for the stronger solutions and extrapolating to zero normality; but we may take this mean value as representing the specific velocity constant of this anhydride for the purpose of comparison with other anhydrides. The temperature-coefficient $K_{25} \div K_{18}$ is 1·575 for 7°,

and hence for 10°, 1·914. The "half-life" period for acetic anhydride is 3′ 58″ at 25° and 6′ 15″ at 18°.

The irregularity at the dilute end of the curves is clearly real, and not due to experimental error. It was observed in both sets of experiments—at 18° and 25°—with different samples of acid and anhydride, in different cells, and with a different conductivity curve in each case; also, as will be seen later, there are indications of the same phenomenon with other anhydrides. It is, however, not easy to see how it is to be explained. A natural suggestion is that it is due to catalytic agents. Now our results indicate clearly that the catalytic influence of hydrogen ion on the hydration of these anhydrides in water is negligible. In our various experiments the concentration of hydrogen ion was varied in the ratio of 8 or 9 to 1, and, as we have shown, the increase was accompanied by an actual fall in the velocity constant. In the same way, Orton and Jones (*loc. cit.*) find that the effect of strong acids is very small in aqueous solution; its greater value in non-aqueous solvents is presumably due to the undissociated acid molecules. On the other hand, hydroxyl ion has a very great catalytic power, as was shown by Orton and Jones, who argue (*loc. cit.*, p. 1715) that our conclusion that the mechanism of hydrolysis of anhydrides must be different from that of esters and amides, is incorrect. The fact, however, still remains that whilst the latter reactions proceed in aqueous solution at a rate proportional to the concentration of hydrogen ion, the former are very nearly, if not quite, independent of this. The influence of hydroxyl ion, on the other hand, seems to be much the same in both series of reactions, although it has not been found possible to measure its effect with any accuracy in the case of anhydrides.* Since in aqueous solution the product of the concentrations of hydrogen and hydroxyl ions is constant, it is obviously not enough to assume that the rate of hydration is proportional to the concentration of hydroxyl ion, and independent of the hydrogen. If this were all, the rate would fall continuously in proportion to the rise of hydrogen ion, owing to the corresponding fall in the hydroxyl ion. The expression for the catalytic influence must be of such a form that the velocity increases when C_{OH} rises above 10^{-7}, but does not fall, or only slightly, when C_{OH} falls below that value, that is, when the solution becomes acid. These conditions are fulfilled by an equation of the form:

$$K' = \alpha + \beta \cdot C_{OH}.$$

If we suppose that α and β are of the same order of magnitude,

* In a subsequent paper it will be shown that the rate of hydration of camphoric anhydride is increased by the presence of hydroxyl ions, and roughly in proportion to the concentration of the latter.

It is obvious that when C_{OH} is high, the first will be negligible in comparison with the second, and hence the velocity will be practically proportional to the concentration of hydroxyl ion (hydroxyl catalysis of the ordinary kind). Where C_{OH} falls below a certain value, the second term will become negligible, and the velocity will not be affected by any further fall in C_{OH}. This is what appears to happen with acetic anhydride. In alkaline solution (that is, when $C_{OH} > 10^{-7}$) the velocity is proportional (more or less) to the hydroxyl ion; but in acid solution ($C_{OH} < 10^{-7}$) it is independent of it. This view also affords a partial explanation of the irregularity observed at the dilute end of the curve. The rapid fall observed up to a concentration of about $N/10$ may possibly be due to the diminution in hydroxyl ions. The rise between $N/10$ and $N/5$ we do not profess to explain.

2.—*Propionic Anhydride.*

Kahlbaum's purest anhydride was used. It was twice distilled, and the fraction boiling at 167—169° was employed.

TABLE VIII.

Hydration of Propionic Anhydride at 25°.

Final norm. of acid.	Initial norm. of anhydride.	K.	$K' = K \times \eta^2/C_w$
0·00830	0·006013	0·000581	0·000583
0·02448	0·02122	600	607
0·06145	0·05163	605	621
0·07852	0·05974	598	617
0·1097	0·08722	586	614
0·1232	0·1010	594	628
0·1510	0·1156	579	619
0·2688	0·2300	580	619
		Mean......	0·000620

TABLE IX.

Hydration of Propionic Anhydride at 18°.

Final norm. of acid.	Initial norm. of anhydride.	K.	$K' = K \times \eta^2/C_w$
0·002668	0·002301	0·000407	0·000407
0·003073	0·002578	409	409
0·01090	0·009227	403	405
0·01662	0·01405	413	415
0·04342	0·03827	412	418
0·06040	0·05115	407	417
0·07250	0·06482	396	408
0·2027	0·1717	383	419
0·1941	0·1756	389	423
0·1981	0·1759	393	429
0·2400	0·2082	383	425
		Mean	0·000419

As before, the last column gives the values of the velocity constant, corrected for the concentration of the water and for the viscosity. These figures show a certain tendency to rise with increasing concentration; but the small range of concentrations examined (owing to the sparing solubility of this anhydride in water) make it difficult to draw any definite conclusions. For the purpose of comparison with other anhydrides, it is desirable to obtain a value for the velocity at infinite dilution, which should be the mean K' if the corrections are justified.

At 25° the mean K' (excluding the first two values) is 0·0006195; the maximum error is 1·4 per cent. At 18° the mean (excluding the first three) is 0·0004191, with a maximum error of 2·8 per cent. The ratio $K'_{25} \div K'_{18}$ is thus 1·48, and hence the temperature-coefficient for 10° is 1·75. The "half-life" period is 8′ 6″ at 25° and 11′ 58″ at 18°.

3.—*Butyric Anhydride (Normal).*

Kahlbaum's "puriss" anhydride was twice distilled, and the fraction boiling at 191—194° was used. The velocity was only measured at 25°.

TABLE X.

Hydration of Butyric Anhydride at 25°.

Final norm. of acid.	Initial norm. of anhydride.	K.
0·007457	0·006757	0·000338
0·01111	0·01032	343
0·01394	0·01225	334
0·03536	0·01651	345
	Mean......	0·000340

The slight solubility of the anhydride makes it impossible to extend the range of concentrations, and hence the correction is too small to be worth applying. The mean value of K is 0·000340, corresponding with a "half-life" period of 14′ 46″.

The maximum initial concentration of the anhydride obtained was about 0·017 equivalent-normal; this may be taken as approximately its solubility in water at 25°.

4.—*Benzoic Anhydride.**

Kahlbaum's "puriss." was twice recrystallised from alcohol. The finely-ground solid was shaken with water at 25°, and the solution filtered into the cell through a plug of glass-wool.

* The measurements of the conductivity of benzoic acid required for these determinations are omitted. Owing to the very high dilutions, they have no absolute value, depending on the nature of the impurities in the water and the size and character of the electrodes.

TABLE XI.

Hydration of Benzoic Anhydride at 25°.

Final norm. of acid.	Initial norm. of anhydride.	K.
0·0000811	0·0000779	0·000158
669	597	163
557	532	160
832	445	152
442	400	155

Mean K 0·000158. "Half-life" period 31′45″.

The anhydride is very sparingly soluble. The highest concen-ration obtained was below 0·00008 equivalent-normal, which may e taken as the solubility in water at 25°. This naturally leads to large experimental error. The highest conductivity measured in ny of the experiments with benzoic anhydride was less than 40 gemmhos.

5.—*Monochloroacetic Anhydride.*

In order to test the influence of negative substituents on the velocity, an attempt was made to measure the rate of hydration of this anhydride. It was prepared by Bischoff and Walden's method (*Ber.*, 1894, **27**, 2949), the acid being distilled in a vacuum with phosphoric oxide. The distillate solidifies to a crystalline mass, melting at 46°. The rate of hydration was found to be far too great for measurement at 18° or 25°. Some of the substance was placed on a glass-wool filter dipping into the cell, which stood in a bath of ice and water. Water cooled to 0° was rapidly drawn through the filter into the cell, which was shaken, and the conduc-tivity measured at once. The first reading was taken within half a minute of the time when the water first came in contact with the anhydride; it is scarcely possible to shorten this period, as the cell must be shaken to make the solution homogeneous. Under hese conditions there were indications of a subsequent rise of con-luctivity, but this did not amount to 5 per cent. If we assume, as an outside estimate, that 5 per cent. of the anhydride was still present after thirty seconds, the value of K would be 0·042 at 0°. At 25° the change must be at least five times as rapid, giving 0·2 as the velocity constant, and 1·5 seconds as the "half-life" period. It thus appears that the replacement of hydrogen by chlorine makes the velocity constant at least one hundred and fifty times as large. The same substitution increases the ionisation constant nearly ninety times.

Conclusion.

The various physical constants we have determined for these acids and their anhydrides are given in the following table. As regards the first two columns, the density and viscosity curves for the acids are so nearly straight that we may assume the increase of density and of viscosity (the values for water at the same temperature being in both cases taken as unity) to be proportional to the normality. These values are also found to be practically the same at 18° as at 25°. The values of the solubility of the anhydrides are only rough, being estimated from the greatest concentrations observed in each case. They are expressed in equivalent normalities.

It will be seen that the introduction of a CH_2 into the acyl group lowers the velocity to about a-half, and the introduction of a chlorine atom increases it more than one hundred and fifty times; whilst the replacement of the methyl in acetic anhydride by phenyl diminishes it to an eighth.

TABLE XII.

Acids.

	$(\Delta-1)/n$.	$(\eta-1)/n$.	$K_{25}\times10^7$.	$K_{18}\times10^7$.
Acetic	0·0082	0·112	187·9	178·8
Propionic.............	0·0060	0·193	122·5	135·8
Butyric	0·0037	0·253	139·7	—
Monochloroacetic ...	—	—	15500	—

Anhydrides.

	$K_{25}\times10^3$.	$K_{18}\times10^3$.	Temp.-coeff. for 10°.	Solubility.
Acetic	1·263	0·802	1·91	2*N* at 18°
Propionic	0·620	0·419	1·75	0·2*N* ,, 18
Butyric............	0·340	—	—	0·017*N* ,, 25
Monochloroacetic	200 ?	—	—	—
Benzoic	0·158	—	—	0·00008*N* ,, 25

Böeseken, Schweitzer, and van der Want have expressed the opinion (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **14**, 622) that a high dissociation constant necessarily implies a high rate of hydration. It is clear, however, that there is no necessary connexion between the two in those anhydrides (such as those which we have examined) where the hydration is not measurably reversible. The results obtained with monobasic acids confirm the conclusions arrived at from the study of the dibasic compounds (see T., 1910, **97**, 1684). The rate of hydration and the dissociation constant show a general tendency to rise and fall together, but

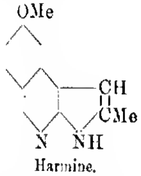
here are exceptions to this rule; and it is clear that whilst some actors tend to increase both, they are not the only factors concerned. A lengthening of the chain, which has little effect on the dissociation, diminishes the rate of hydration; the introduction of the heavy phenyl group, although it causes a marked increase in the ionisation, still further diminishes the reaction constant; but a chlorine atom, which enormously increases the dissociation constant with a comparatively small change in the structure and weight of the molecule, produces a correspondingly large rise in the rate of hydration.

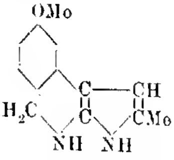
DAUBENY LABORATORY
MAGDALEN COLLEGE, OXFORD.

CCIX.—*Harmine and Harmaline. Part II. The Synthesis of* iso*Harman.*

By WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON.

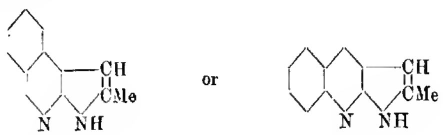
IN Part I of this investigation of the constitution of harmine and harmaline (T., 1912, **101**, 1775) we were able to show that these substances, in all probability, are derivatives of *iso*quinoline, and that their constitutions are probably represented by the formulæ:


Harmine.


Harmaline.

We, however, thought it desirable to obtain further evidence in support of the *iso*quinoline structure of these substances, and, in the present communication, we describe synthetical experiments undertaken with this object in view. O. Fischer (*Chem. Centr.*, 1901, i, 957) has shown that the methoxy-group in harmine may be eliminated by the following series of reactions. Harmine is converted by the action of hydrochloric acid at 140–170° into harmol, the methyl group being eliminated in the usual manner, and when harmol is heated with zinc chloride ammonia it yields aminoharman by the replacement of the hydroxy- by the amino-group. Lastly, the amino group in aminoharman may be replaced

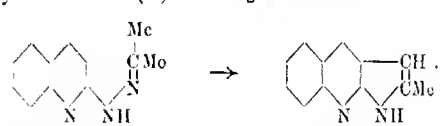
by hydrogen by the aid of the diazo-reaction, and the substance thus obtained has been named "*harman.*" The problem in connexion with the constitution of harman is the same as that which we have mentioned in the case of harmine and harmaline; it is necessary to decide whether harman is a derivative of *iso*quinoline or of quinoline, that is to say, whether its structure is to be represented by (I) or by (II):



(I.) or (II.)

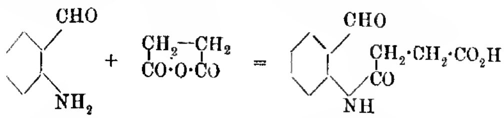
It is clear that, if this point is definitely decided in the case of harman, there can no longer be any doubt as to the *iso*quinoline or quinoline structure of harmine and harmaline. It seemed to us that this matter might best be decided by synthesising one of the substances just represented, and we selected the quinoline derivative (II) because it was thought that its synthesis would probably present less difficulty than that of the *iso*quinoline derivative (I).

Substance (II) is an indole derivative, in which the benzene ring is replaced by quinoline, and is therefore somewhat similarly constituted to 2-methylindole, and the most obvious process for its synthesis seemed to be the application of the Emil Fischer indole synthesis to *acetone-2-quinolylhydrazone*, which should yield substance (II) according to the scheme:

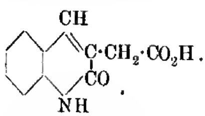


We therefore prepared acetone-2-quinolylhydrazone by the condensation of acetone with 2-quinolylhydrazine, but all attempts to convert it into the indole derivative by heating with hydrochloric acid, zinc chloride, or other condensing agents were unsuccessful, hydrolysis occurring in most of the experiments. As the only other method of attack seemed to be to build up the substance of formula II from a simpler starting point, we experimented in this direction, and ultimately accomplished the synthesis in the following manner. In the first place, *o-aldehydosuccinanilic acid*

(m. p. 115°) was prepared by condensing *o*-aminobenzaldehyde with succinic anhydride in boiling xylene solution:

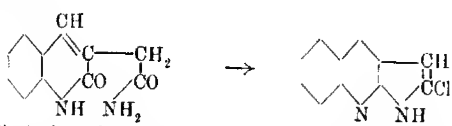


The aqueous solution of the sodium salt of this anilic acid was then digested with weak alkali, when internal condensation took place with the formation of *carbostyril-3-acetic acid* (m. p. 270°),



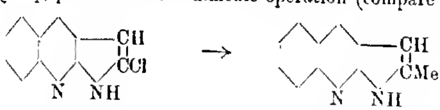
a condensation which closed the second ring of the formula.

The acid was then converted into the methyl ester (m. p. 175°), and this into the amide (m. p. 258°), which, when boiled with phosphoryl chloride, undergoes a remarkable reaction, which closes the third ring of the formula, and *chloronor*iso*harman* (m. p. 127°) is produced:



Amide of carbostyril-3-acetic acid. Chloronor*iso*harman.

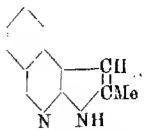
The last step in the synthesis of *iso*norharman, namely, the replacement of the chlorine atom in chloronor*iso*harman by the methyl group, proved to be a difficult operation (compare p. 1984),



*iso*Harman.

but it was ultimately accomplished by adding the chloro-derivative to a solution of magnesium methyl iodide in boiling *iso*amyl ether. iso*Harman* crystallises well from methyl alcohol, and melts at 213–215°, and although it has properties which are, as indeed might be expected, strikingly similar to those of harman (m. p. 230°), it is certainly not identical with that substance, and it follows, therefore, that harman cannot be this quinoline deriv-

ative, but must have the *iso*quinoline structure represented by the formula:



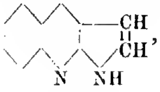
There can therefore be little doubt that the constitutional formulæ for harmine and harmaline suggested at the commencement of this communication do, in fact, actually represent these substances.

When chloronor*iso*harman is digested in acetic acid solution with dry potassium acetate it undergoes a curious decomposition, and is converted into a substance melting at 235°, which is evidently either hydroxynor*iso*harman, the lactim, or more probably the corresponding *lactam* of *2-aminoquinoline-3-acetic acid*:

A series of experiments were made in the hope that this substance might react with magnesium methyl iodide to yield hydroxydihydro*iso*harman,

from which *iso*harman should result by the elimination of water, but the process did not take place under the conditions we employed.

During the course of these experiments it was thought that it would be interesting to reduce chloronor*iso*harman, and thus to obtain *norisoharman* or *12-quinindole*,* the parent substance of *iso*harman, and this was found to be a much more difficult matter



than we had anticipated, since most of the usual reducing agents failed to produce the desired result, but ultimately we were able to bring about the reduction by using tin and hydrochloric acid

* For an explanation of the nomenclature of this substance, see T., 1912, 101, 1787.

at the ordinary temperature under the conditions described on p. 1983.

12-*Quinindole* appears to be the first representative of this class of substance; it melts at 85°, and is a strong base, which yields readily soluble and stable salts. It has little similarity to its 2-methyl derivative (*iso*harman), which melts at a much higher temperature (215°), is much less soluble in organic solvents, and yields salts which are also much less soluble than those of 12-quinindole.

It does not often happen that the mere substitution of hydrogen by methyl produces such a striking modification in the properties of the parent substance.

Experimental.

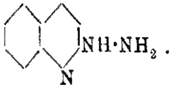
1-*Methylquinolone*, 2-*Chloroquinoline*, and 2-*Quinolylhydrazine*.

1-Methylquinolone has already been prepared from carbostyril by methylation in methyl-alcoholic solution with methyl iodide in the presence of sodium hydroxide (Friedländer and Müller, *Ber.*, 1887, **20**, 2009), and by the oxidation of quinoline methiodide with potassium ferricyanide (Decker, *J. pr. Chem.*, 1893, [ii], **47**, 31; compare also Ostermayer, *Ber.*, 1885, **18**, 594, and Bernthsen and Hess, *ibid.*, 37); also by the action of potassium hydroxide on 2-iodoquinoline methiodide (Roser, *Annalen*, 1894, **282**, 377), but we have found that a more convenient method of preparation than any of these is the following. Methyl sulphate (50 grams) is gradually added to quinoline (50 grams), the vigorous reaction being controlled by cooling with water; the solid product is dissolved in water, mixed with a solution of freshly-recrystallised potassium ferricyanide (300 grams), and the whole made up to 2500 c.c. with water and transferred to a bottle. A considerable quantity of ether is poured in, and then potassium hydroxide (10 per cent.) added in small quantities at a time until the liquid is strongly alkaline, the whole being well shaken after each addition. The bottle is then shaken for ten minutes on the machine, the colourless ethereal solution separated, washed, dried over anhydrous potassium carbonate, and evaporated, when a solid residue of nearly pure 1-methylquinolone is obtained, the yield being 55 grams, or 90 per cent. of that theoretically possible.

The substance may be purified by recrystallisation from light petroleum, from which it separates in needles melting at 74° and having a pleasant aromatic odour.

2-*Chloroquinoline*.—The conversion of 1-methylquinolone into 2-chloroquinoline, a change which takes place with the elimination

of the methyl group, has been described by O. Fischer (*Ber.*, 1898, **31**, 612), who heated methylquinolone with a mixture of phosphorus pentachloride and phosphoryl chloride for eight hours at 130—140°, but we find that a higher temperature is necessary. 1-Methyl-quinolone (54 grams) is heated with phosphorus pentachloride (100 grams) and phosphoryl chloride (50 grams) for nine hours in an oil-bath kept at 175°. The hydrochloride of methylquinolone, which separates at first as a solid, soon liquefies, and the homogeneous liquid is distilled until the phosphoryl chloride has passed over and the excess of pentachloride commences to sublime; the residue is then carefully decomposed by water, excess of potassium hydroxide is added, and the whole distilled in steam. The distillate is extracted with ether, the ethereal solution dried over solid potassium hydroxide, evaporated, and the chloroquinoline distilled, when it passes over at 268°/744 mm., crystallises, and melts at 38°, the yield being 85—90 per cent. of that theoretically possible.

2-Quinolylhydrazine, 

This substance was first prepared by Marckwald and Meyer (*Ber.*, 1900, **33**, 1885), who obtained it, together with 2-hydrazoquinoline, by heating 2-chloroquinoline with a large excess of hydrazine hydrate at 140° for six hours in sealed tubes. As we required considerable quantities of this substance, we endeavoured to improve this troublesome method of preparation, and find that 2-quinolylhydrazine is produced almost quantitatively when a mixture of 2-chloroquinoline (12 grams) and hydrazine hydrate (50 grams) is boiled in a flask with a ground-in condenser on the sand-bath for an hour. The orange-yellow liquid is distilled under diminished pressure until the excess of hydrazine hydrate has been recovered, the residue mixed with hot water, when the hydrazine soon separates in orange crystals, and after one crystallisation from benzene melts at 142—143°. The yield is 11 grams, and the substance is quite free from 2-hydrazoquinoline.

Acetone-2-quinolylhydrazone, $C_9H_6N\cdot NH\cdot N{:}CMe_2$.—In order to prepare this substance, 2-quinolylhydrazine is dissolved in excess of acetone, and, after remaining for five minutes, water is carefully added, and the whole well rubbed with a glass rod, but crystallisation is much facilitated by the addition of a crystal from a previous operation. The solid mass is collected and recrystallised from light petroleum (b. p. 50—60°), from which the substance

eparates in stout, pale yellow, prismatic needles, which melt at 00° with slight previous softening:

0·1177 gave 0·3138 CO_2 and 0·0712 H_2O. C=72·7; H=6·7.
0·1171 „ 21·2 c.c. N_2 at 16° and 756 mm. N=21·1.
$C_{12}H_{13}N_3$ requires C=72·4; H=6·5; N=21·1 per cent.

Experiments made with the object of converting this substance into *iso*harman (compare p. 1974) by heating with zinc chloride according to Emil Fischer's method, were unsuccessful, since, although the conditions were greatly varied, the only product which could be isolated was the zinc chloride double salt of quinolylhydrazine. Acid reagents, such as sulphuric acid or concentrated aqueous hydrochloric or hydrobromic acids, simply hydrolyse the substance to acetone and quinolylhydrazine without any internal condensation taking place, but the cause of the failure is still being investigated.

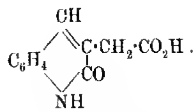
o-Aldehydosuccinanilic Acid, $CHO{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$.

The best conditions for the preparation of this substance seem to be the following. Pure succinic anhydride (20 grams) is dissolved in carefully dried, boiling xylene (200 c.c.), the lamp removed, and then *o*-aminobenzaldehyde (24 grams) * added all at once. The liquid boils, and, on keeping, soon clouds, and deposits a nearly colourless, syrupy layer, which solidifies overnight, and crystals also separate in quantity from the xylene solution. The xylene is decanted, the crystals washed with benzene, and recrystallised from methyl ethyl ketone, from which the anilic acid separates in crusts of glistening prisms. The xylene solution, after concentration under diminished pressure, yields a further small quantity of the same substance, the total yield being about 80 per cent. of that theoretically possible:

0·1483 gave 0·3252 CO_2 and 0·0688 H_2O. C=59·8; H=5·1.
0·1334 „ 0·2927 CO_2 „ 0·0622 H_2O. C=59·7; H=5·2.
0·1429 „ 8·0 c.c. N_2 at 13° and 747 mm. N=6·5.
$C_{11}H_{11}O_4N$ requires C=59·7; H=5·0; N=6·3 per cent.

o-Aldehydosuccinanilic acid melts at 114—115°, and dissolves readily in most organic solvents; it is sparingly soluble in cold, but dissolves somewhat in boiling water, and separates on cooling in long, glistening, colourless needles.

* For the preparation of *o*-aminobenzaldehyde, by the reduction of *o*-nitrobenzaldehyde with ferrous sulphate and ammonia, see Friedländer (*Ber.*, 1882, **15**, 2572; 1884, **17**, 456). We are greatly indebted to the Farbwerke vormals Meister, Lucius & Brüning for generously supplying us with all the *o*-nitrobenzaldehyde required for this investigation.

Carbostyril-3-acetic Acid, 

The formation of this substance from *o*-aldehydosuccinanilic acid by internal condensation takes place under the influence of small quantities of alkali, but even when special conditions are observed the yield may vary greatly, and sometimes hydrolysis of the anilic acid may occur to so large an extent that only very small quantities of the carbostyrilacetic acid are produced. The following two processes have been employed with success in the preparation of this substance.

I. Succinanilic acid (5 grams), which must be quite pure, is dissolved in water (100 c.c.) and sodium carbonate (2·5 grams), the solution gradually heated to boiling in a reflux apparatus, and then boiled for four hours. The product is mixed whilst still hot with excess of hydrochloric acid, and allowed to remain for twenty-four hours, when a sandy, crystalline precipitate (3·5 grams) of crude carbostyrilacetic acid separates.

II. Pure succinanilic acid (5 grams) is dissolved in water (150 c.c.) and a slight excess of sodium carbonate; 1 c.c. of a 50 per cent. solution of sodium hydroxide is then added, and the solution heated to boiling in a reflux apparatus for two hours. The hot product is acidified, the precipitate (3·5 grams) of crude carbostyrilacetic acid collected, washed with dilute hydrochloric acid, and drained on porous porcelain.

The crude acid is best purified by dissolving in the minimum quantity of glacial acetic acid, in which it is sparingly soluble, filtering, and then adding half the volume of boiling water, when the pure substance separates as a sandy powder, which, under the microscope, is seen to consist of small prisms:

0·1281 gave 0·3050 CO_2 and 0·0530 H_2O. C=64·9; H=4·6.
0·1411 ,, 8·5 c.c. N_2 at 14° and 756 mm. N=7·0.
$C_{11}H_9O_3N$ requires C=65·0; H=4·4; N=6·9 per cent.

Carbostyril-3-acetic acid melts and decomposes at about 268—270°, and is very sparingly soluble in alcohol, acetone, chloroform, or toluene; it is almost insoluble in cold water, and very sparingly so on boiling, and separates on cooling as a sandy mass of quite colourless crystals.

The *methyl* ester, $C_{10}H_8ON{\cdot}CO_2Me$, is obtained in almost quantitative yield by boiling the acid (5 grams) with methyl alcohol (100 c.c.) and sulphuric acid (10 c.c.), the acid gradually passes

into solution, and, after boiling for three hours in a reflux apparatus on the steam-bath, the solution is allowed to cool, when it becomes filled with a mass of needles of the methyl ester, and a considerable further quantity is precipitated by dilution with two volumes of water. The whole is collected, washed with water, drained on porous porcelain, and recrystallised from methyl alcohol:

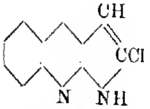
0·1435 gave 0·3485 CO_2 and 0·0671 H_2O. C=66·2; H=5·2.
$C_{12}H_{11}O_3N$ requires C=66·3; H=5·1 per cent.

Methyl carbostyril-3-acetate melts at 175°, is readily soluble in boiling alcohol or acetone, and crystallises well from both these solvents; it is also readily soluble in hot chloroform or toluene, but sparingly so in light petroleum.

The *amide*, $C_{10}H_8ON{\cdot}CO{\cdot}NH_2$, may be prepared by heating the methyl ester with a large excess of saturated aqueous ammonia in a sealed tube in the steam-bath for three hours, the whole being then thoroughly shaken and the heating continued for a further six hours. The colourless, granular, crystalline cake is collected, ground up, washed well with water, and the residual, almost pure amide crystallised from dilute acetic acid:

0·1231 gave 0·2969 CO_2 and 0·0591 H_2O. C=65·7; H=5·3.
0·1440 „ 13·7 c.c. N_2 at 14° and 748 mm. N=13·9.
$C_{11}H_{10}O_2N_2$ requires C=65·3; H=4·9; N=13·8 per cent.

Carbostyril-3-acetamide melts at about 258°, and decomposes with evolution of gas at 265—270°; it is very sparingly soluble in alcohol, acetone, or toluene, and in cold acetic acid, but it dissolves readily in boiling acetic acid, and the solution, diluted with three volumes of water, gradually deposits the pure amide in groups of microscopic needles. The ammoniacal filtrate from the preparation of the amide yields, after boiling away the ammonia and acidifying, a crystalline precipitate of pure carbostyril-3-acetic acid.

Chloronorisoharman,  .

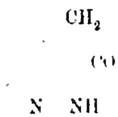
This substance is obtained almost quantitatively when carbostyril-3-acetamide is heated with phosphoryl chloride. The amide (2 grams), mixed with phosphoryl chloride (5 c.c.), is heated in a test-tube by means of a sulphuric acid bath, when it gradually dissolves with the evolution of hydrogen chloride. After keeping at 80° and shaking until all has dissolved, the temperature is

gradually raised, and most of the excess of phosphoryl chloride distilled out of the test-tube. The dark brown residue is then stirred with water and ice, when a yellow, caseous precipitate separates, which is collected, washed well, drained on porous porcelain, and recrystallised from dilute acetic acid:

0·1341 gave 0·3204 CO_2 and 0·0437 H_2O. C=65·1; H=3·6.
0·1492 ,, 0·1054 AgCl. Cl=17·5.
0·1245 ,, 15·1 c.c. N_2 at 17° and 753 mm. N=14·0.
$C_{11}H_7N_2Cl$ requires C=65·1; H=3·5; N=13·8; Cl=17·5 per cent.

Chloronorisoharman melts at 128° to a pale yellow liquid with a green fluorescence. It is readily soluble in boiling alcohol, acetone, chloroform, or benzene, very sparingly so in light petroleum, and separates from a mixture of the latter with benzene in characteristic, lemon-yellow stars; from dilute acetic acid it crystallises in pale yellow leaflets. It dissolves in sulphuric acid, yielding an almost colourless solution, and in concentrated hydrochloric acid with the formation of a salt which is dissociated by water. When a trace is dissolved in boiling quinoline, the solution has an intense green fluorescence very similar to that of fluorescein. It dissolves in dilute methyl-alcoholic potassium hydroxide, and, on warming, a deep crimson solution is produced, but on shaking with air the colour disappears; if water is added to the crimson solution it becomes green, and gradually deposits a crystalline precipitate.

The Lactam (or Lactim) of 2-Aminoquinoline-3-acetic Acid.

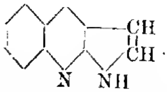


This substance is produced when chloronor*iso*harman (5 grams), dissolved in glacial acetic acid (30 c.c.), is boiled with dry potassium acetate (10 grams); potassium chloride is gradually deposited, and, after two hours, dilution with water causes the lactam to separate as a nearly colourless precipitate. This is collected, washed well, and recrystallised from dilute acetic acid, from which it separates in lemon-yellow, prismatic needles:

0·1468 gave 0·3854 CO_2 and 0·0601 H_2O. C=71·6; H=4·4.
0·1615 ,, 0·4312 CO_2 ,, 0·0662 H_2O. C=72·1; H=4·5.
0·1293 ,, 16·5 c.c. N_2 at 10° and 732 mm. N=14·7.
$C_{11}H_8ON_2$ requires C=71·7; H=4·3; N=15·2 per cent.

The *lactam of 2-aminoquinoline-3-acetic acid* melts at 235°, and is sparingly soluble in the usual organic solvents, yielding solutions

iich have a pale green fluorescence. When the solution in 30 per nt. sulphuric acid is boiled, hydrolysis occurs, and, on adding ter, a substance separates, which melts at about 268°, is readily uble in dilute sodium carbonate, and is therefore doubtless rbostyril-3-acetic acid.

*Nor*iso*harman*(-12-*quinindole*), 

The difficulty experienced in reducing chloronor*iso*harman to r*iso*harman has been referred to in the introduction (p. 1976), d the change was ultimately brought about under the following nditions.

The chloro-derivative (11 grams) is ground to a thin paste with ncentrated hydrochloric acid (100 c.c.); granulated tin 0 grams) is then added in small quantities at a time, and the hole repeatedly shaken, when, after about a week, almost the hole of the substance will have dissolved. The tin salt, which will ve separated in small quantity, is brought into solution by adding equal volume of water and heating on the steam-bath; the ole is then filtered, and set aside in the ice chest to crystallise. e tin salt is then collected, washed, dissolved in hot water, and composed by hydrogen sulphide.

After filtering, the filtrate is evaporated to a small bulk, made rongly alkaline with ammonia, when an oil separates, which immeately crystallises, and a further quantity is obtained from the other liquor by the addition of excess of sodium hydroxide. The bstance is collected and recrystallised from light petroleum . p. 60—70°), in which nor*iso*harman is sparingly soluble in the ld, and from which it separates in colourless, glistening, featherv oups of needles:

0·0902 gave 0·2584 CO_2 and 0·0406 H_2O. C=78·3; H=4·8.
0·1002 „ 0·2879 CO_2 „ 0·0437 H_2O. C=78·3; H=4·8.
0·1037 „ 15·1 c.c. N_2 at 15° and 715 mm. N=16·8.

$C_{11}H_8N_2$ requires C=78·5; H=4·8; N=16·7 per cent.

*Noriso*harman melts at 84—85°, and is readily soluble in the mmon organic solvents; it dissolves in concentrated sulphuric id, and the colourless solution has a pale blue fluorescence. It is powerful base, which dissolves readily even in very dilute hydroloric acid, and the solution gives, on the addition of mercuric loride, a voluminous precipitate consisting of long, slender edles. This *mercurichloride* dissolves in much boiling water, and parates on cooling in nodular groups of needles. The *platini-*

chloride, $(C_{12}H_{10}N_2)_2H_2PtCl_6$, separates, on the addition of platinic chloride to the cold dilute solution of the hydrochloride, as a voluminous, drab precipitate, which is sparingly soluble in cold water, but dissolves in much boiling water, and separates, on keeping, as a glistening, pale yellow powder, consisting of well-defined, microscopic prisms:

0·1648 gave 0·2130 CO_2 and 0·0396 H_2O. C = 35·3; H = 2·4.

0·3784 „ 0·1007 Pt. Pt = 26·4.

$(C_{11}H_8N_2)_2H_2PtCl_6$ requires C = 35·4; H = 2·4; Pt = 26·2 per cent.

iso*Harman* (2-*Methyl*-12-*quinindole*), 

The first attempts to prepare this substance were by the action of zinc methyl on chloronor*iso*harman, but, although a variety of conditions were employed, the results were always unsuccessful, and this is the more remarkable since chloronor*iso*harman is readily soluble in zinc methyl. In one experiment this substance (2 grams), dissolved in zinc methyl (5 grams), was heated in a sealed tube in the steam-bath; the solution became brown, and a brown film formed on the side of the tube.

After an hour the zinc methyl was boiled away, and the residue treated with dilute hydrochloric acid, but no base separated from the filtered solution on the addition of ammonia. The action of magnesium methyl iodide in ethereal solution proved also to be unsuccessful, probably on account of the sparing solubility of chloronor*iso*harman in that solvent, but ultimately, by employing *iso*amyl ether instead of ordinary ether, we succeeded in obtaining small quantities of *iso*harman.

Magnesium (4 grams), covered with *pure iso*amyl ether, was mixed with methyl iodide (24 grams) and gently heated to start the reaction, and, when this slackened, the whole was heated to boiling, and then chloronor*iso*harman (5 grams) added all at once. On heating, the liquid soon clouds, and, after two hours, the product was decomposed by water, the *iso*amyl ether removed by distillation in steam, the residue mixed with excess of dilute hydrochloric acid and a considerable amount of tar removed by filtration. The filtrate was made strongly alkaline with ammonia, and extracted on the machine with much ether; the ethereal solution was dried over potassium carbonate, evaporated to a small bulk, when, on keeping, nearly pure *iso*harman (0·2 gram) separated as a brown, crystalline mass. This was dissolved in dilute hydrochloric acid,

ltered from a trace of insoluble, brown impurity, reprecipitated by lkali, and recrystallised from methyl alcohol:

0·1010 gave 0·2914 CO_2 and 0·0527 H_2O. C=78·7; H=5·8.
0·0984 „ 0·2843 CO_2 „ 0·0522 H_2O. C=78·9; H=5·9.
0·1052 „ 14·3 c.c. N_2 at 16° and 752 mm. N=15·7.
$C_{12}H_{10}N_2$ requires C=79·1; H=5·5; N=15·4 per cent.

iso*Harman* is readily soluble in hot methyl alcohol, and separates n slowly cooling in almost colourless leaflets. It melts at 13—215°, and, when heated in small quantities in a test-tube, it ublimes almost without decomposition. The solution in sulphuric cid exhibits a bluish-violet fluorescence. The salts are highly rystalline, and much less soluble than those of nor*iso*harman; the ydrochloride crystallises readily from water in slender, yellow eedles, and the *mercurichloride* in long needles. The *picrate* is paringly soluble in most solvents, but may be crystallised from nethyl ethyl ketone, from which it separates in yellowish-green eedles, which darken above 240°, and melt and decompose at bout 253°. The properties of *iso*harman are therefore strikingly milar to those of harman, which also sublimes, is readily soluble n alcohol, and dissolves in sulphuric acid to a bluish-violet uorescent solution. Harman melts, however, at 230°, and appears o be more soluble in water than *iso*harman.

Moreover, aqueous solutions of the salts of harman exhibit a blue uorescence, whereas the corresponding salts of *iso*harman do not ppear to fluoresce. It is therefore clear that harman and oharman are different substances.

We wish to state that much of the expense of this investigation as defrayed by a grant from the Research Fund of the Royal ociety, and to express our thanks to Prof. W. R. Dunstan for indly obtaining a supply of the seeds of *Peganum harmala*, and o Messrs. Burroughs, Wellcome, and Co. for undertaking the xtraction of the alkaloids.

THE UNIVERSITIES OF OXFORD AND MANCHESTER.

CCX.—*The Action of Nitrogen Iodide on Methyl Ketones.*

By FREDERICK DANIEL CHATTAWAY and ROBERT REGINALD BAXTER.

KETONES containing a methyl group react very readily with nitrogen iodide, iodoform, ammonia, an acid, and an amide being produced. In these reactions the methyl group appears first to be completely substituted by iodine, a tri-iodomethyl ketone being formed, which in presence of the ammonia simultaneously set free is hydrolysed to iodoform and an acid, a similar reaction between the substituted ketone and ammonia leading to the formation of iodoform and an amide.

The reactions may be formulated thus:

$$R\cdot CO\cdot CH_3 + NH_3\cdot NI_3 = R\cdot CO\cdot CI_3 + 2NH_3.$$
$$R\cdot CO\cdot CI_3 + H_2O + = R\cdot CO_2H + CHI_3.$$
$$R\cdot CO\cdot CI_3 + NH_3 = R\cdot CO\cdot NH_2 + CHI_3.$$

Interaction of Nitrogen Iodide and Acetophenone.

To a quantity of nitrogen iodide suspended in a dilute aqueous solution of ammonia an excess of acetophenone was added, and the mixture vigorously shaken for some hours. The nitrogen iodide gradually disappeared, and the excess of acetophenone, together with the solid product of the action, collected into brown, semi-crystalline lumps. The aqueous layer, having been filtered off through several wetted filter papers, was extracted with ether, and the residue after the first extraction, having been made acid with dilute sulphuric acid, was again extracted with ether. The ethereal extracts were evaporated, and the white solid residues recrystallised from alcohol. The compound extracted from the alkaline liquid proved to be benzamide, and the extract from the acidified residue, benzoic acid. The semi-solid lumps were separated by a filter-pump into a crystalline solid and a heavy brown oil. The solid proved to be iodoform, which was obtained quite pure by one crystallisation from alcohol. The oil consisted of acetophenone, together with a small quantity of some compound containing a large percentage of iodine, possibly the undecomposed tri-iodoacetophenone which must be formed during the reaction; it was, however, obtained in too small an amount to admit of isolation. The reaction probably takes place first by the replacement of hydrogen atoms of the methyl group by iodine, thus:

$$CH_3\cdot CO\cdot C_6H_5 + NH_3\cdot NI_3 = CI_3\cdot CO\cdot C_6H_5 + 2NH_3.$$

The intermediate product then reacts with water, thus:

$$CI_3\cdot CO\cdot C_6H_5 + H_2O = CHI_3 + C_6H_5\cdot CO_2H,$$

.nd to a smaller extent with ammonia, thus:

$$CI_3\cdot CO\cdot C_6H_5 + NH_3 = CHI_3 + C_6H_5\cdot CO\cdot NH_2.$$

Interaction of Nitrogen Iodide and Acetone.

The action of acetone on nitrogen iodide is very striking, since he black compound in the course of a few minutes is apparently ransformed into a bright yellow one. Nitrogen iodide, obtained n a state of fine division by adding a solution of iodine mono-hloride in hydrochloric acid to strong ammonia, was suspended in dilute solution of ammonia (20 c.c. of concentrated ammonia in 100 c.c. of water), and about its own weight of acetone added. The flask was shaken at intervals for about fifteen minutes until he black nitrogen iodide had completely disappeared, and its place had been taken by a yellow solid, which proved to be iodoform. The solution was boiled, to expel the excess of acetone and of ammonia, and lead oxide was added to the hot liquid until lead odide was no longer formed. After cooling, the lead iodide was iltered off, and the filtrate made slightly acid with dilute sulphuric acid. After removing a little lead sulphate, the liquid was distilled, when acetic acid was found in the distillate.

The course of the reaction is undoubtedly similar to that which akes place with acetophenone, but here the acetamide, which probably is formed in small quantity, cannot be isolated.

Preparation of Iodoform.

The method of preparing iodoform ordinarily used in the labora-tory, that is, adding iodine to a warm solution of an alkaline carbonate containing ethyl alcohol or acetone, is not at all satis-factory. The yield of iodoform never reaches more than about one-sixth of the weight of iodine used, and may be much less. Part of the iodine lost can, it is true, be recovered from the alkaline mother liquor after separation of the iodoform, although when working on a small scale the amount thus obtained is seldom worth the time and trouble involved.

The interaction of nitrogen iodide and acetone above described affords a means of increasing at least fourfold the yield of iodoform from a given quantity of iodine. By the following procedure about four-fifths of the iodine used can be obtained in the form of iodoform.

A mixture of 40 c.c. of concentrated hydrochloric acid and 4 c.c.

of concentrated nitric acid is gently warmed in an open dish, and 10 grams of finely powdered iodine are gradually added. When the solid iodine has disappeared, the mixture is boiled gently for five minutes, more hydrochloric acid being added to keep up the bulk as the liquid evaporates. No appreciable amount of vapour of iodine monochloride should be given off.

Eighty c.c. of concentrated aqueous ammonia are poured over not less than 200 grams of crushed ice, the mixture is cooled in a freezing machine, and the cooled solution of iodine monochloride is added drop by drop, stirring vigorously during the addition. The nitrogen iodide, separated by a filter-pump and washed several times with concentrated ammonia, is, while still moist and perfectly safe to handle, transferred to a beaker and stirred to a paste with about 20 c.c. of concentrated aqueous ammonia. Ten c.c. of acetone are then immediately added, and the mixture is left, without cooling, until the black nitrogen iodide disappears and a yellow paste of iodoform takes its place. This generally occurs in about five minutes, the temperature of the liquid rising to about 40°. Water is added, the iodoform washed once or twice by decantation, and dissolved in boiling alcohol; usually about 80—100 c.c. of alcohol are needed. A clear, yellow solution is thus obtained, from which, on cooling, 7—8 grams of pure iodoform separate in yellow, hexagonal plates. A further 1—2 grams of iodoform can be obtained by adding water to the alcoholic mother liquor.

University Chemical Laboratory,
Oxford.

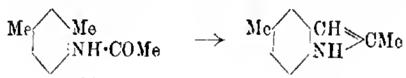
CCXI.—*Researches on the Constitution of Physostigmine. Part III. The Formation of Substituted Indoles from* m-4-*Xylidine, and the Reduction of 3-Nitro*-p-*tolylacrylic Acid.*

By Arthur Henry Salway.

In continuation of the author's previous investigations (T., 1912, **101**, 978; **103**, 351) on physostigmine (eserine), $C_{15}H_{21}O_2N_3$, some synthetic experiments have been conducted with the object of obtaining a further insight into the constitution of the alkaloid. Although these experiments have not resulted in the synthesis of the desired compounds, and are of no value for the solution of the

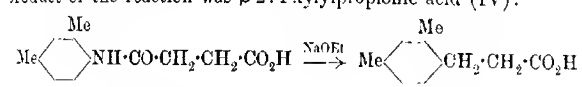
roblem under consideration, they are not entirely devoid of iterest, and it is therefore proposed to place them on record, and describe the characters of the new compounds which have been repared.

It has recently been shown by Madelung (*Ber.*, 1912, **45**, 1128, 541) that *o*-toluidides, $C_6H_4<^{NH\cdot CO\cdot R}_{Me}$, can be converted into ndole derivatives, $C_6H_4<^{NH}_{CH}\geqslant C\cdot R$, by heating with dry sodium thoxide. By applying such a reaction to acyl derivatives of n-4-xylidine it was thought that substituted 5-methylindoles might be obtained, and a suitable choice of the acyl radicle would enable one to prepare compounds of service in helping to elucidate the constitution of physostigmine. Consequently it was necessary, in the first place, to ascertain whether the simplest xylidides could be converted by the above method into indole derivatives, and accordingly aceto-*m*-4-xylidide (I) was investigated in this direction, when a good yield of 2:5-dimethylindole (II) was obtained:



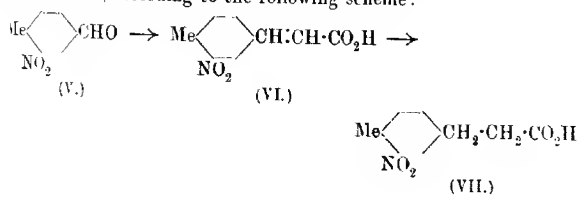
(I.) (II.)

Unfortunately, the reaction was not generally applicable to other lerivatives of *m*-4-xylidine, since the compound of chief interest to he author, namely, 2:4-*xylylsuccinamic acid* (III), suffers disruption under the influence of dry sodium ethoxide, and the principal product of the reaction was β-2:4-xylylpropionic acid (IV):



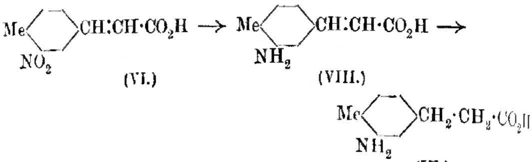
(III.) (IV.)

The second part of this investigation arose out of an attempt to prepare β-3-nitro-*p*-tolylpropionic acid (VII). For this purpose p-tolualdehyde was first nitrated, and the resulting *m*-nitro-*p*-toluldehyde (V) converted into 3-nitro-*p*-tolylacrylic acid (VI); it was hen assumed that the latter would yield the required compound on reduction, according to the following scheme:



(V.) (VI.) (VII.)

It was observed, however, that the nitro-group of 3-nitro-*p*-tolyl-acrylic acid (VI) was more readily attacked by reducing agents than the cinnamyl residue, so that the first product of the reaction was not a substituted propionic acid (VII), but 3-*amino*-p-*tolylacrylic acid* (VIII), which by further reduction then became converted into *β-3-amino*-p-*tolylpropionic acid* (IX):



(VI.) (VIII.) (IX.)

Under no condition of reduction investigated by the author was it possible to reduce the 3-nitro-*p*-tolylacrylic acid (VI) without affecting the nitro-group.

Experimental.

I. *Preparation of 2:5-Dimethylindole from* m-4-*Xylidine*.

In order to ascertain whether *m*-4-xylidine could be converted into 2:5-dimethylindole, a quantity of the former was acetylated, and the resulting acetyl derivative (m. p. 129°; b. p. 170°/10 mm.) heated for a short time at 250—300° with an equal weight of dry sodium ethoxide in the absence of air. After the vigorous reaction which ensued had subsided, water was added, and the mixture distilled in a current of steam. The first portion of the distillate contained xylidine, but subsequently a solid compound began to pass over into the receiver. This was collected separately, and purified by crystallisation from a mixture of benzene and light petroleum, when glistening leaflets melting at 114° were obtained (Found, C=82·7; H=7·7. $C_{10}H_{11}N$ requires C=82·8; H=7·6 per cent.). This substance readily gave the pine-shaving colour reaction typical of indoles, and was evidently identical with 2:5-dimethylindole (compare Raschen, *Annalen*, 1887, **239**, 227). The yield of the latter amounted to 40 per cent. of the acetoxylidide employed in the reaction.

2:4-*Xylylsuccinamic Acid* (III, p. 1989).

For the preparation of this compound six parts of *m*-4-xylidine were added to a solution of five parts of succinic anhydride in hot chloroform, and the mixture allowed to cool. In a very short time colourless, slender needles of the succinamic acid were deposited, the yield amounting to 80 per cent. of the theoretical. The sub-

stance was collected and purified by crystallisation from chloroform, when it was found to sinter at 160° and to become completely melted at 164°:

0·0965 gave 0·2299 CO_2 and 0·0614 H_2O. C=65·0; H=7·1.

0·1063 required for neutralisation 4·85 c.c. *N*/10-KOH. Neutralisation Value=256.

$C_{12}H_{15}O_3N$ requires C=65·2; H=6·8 per cent. Neutralisation Value=254.

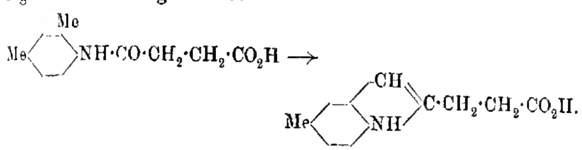
2:4-*Xylylsuccinamic acid* is readily soluble in alcohol, but only moderately so in chloroform, benzene, or hot water. Its *methyl* ester, prepared by heating the substance for about fifteen minutes * with methyl alcohol saturated with hydrogen chloride, crystallises from a mixture of benzene and light petroleum in colourless needles melting at 107°.

Found: C=66·7; H=7·2.

$C_{13}H_{17}O_3N$ requires C=66·4; H=7·2 per cent.

Action of Sodium Ethoxide on 2:4-Xylylsuccinamic Acid. Formation of β-2:4-Xylylpropionic Acid.

The object of this experiment was to ascertain whether 2:4-xylylsuccinamic acid could be converted into an indole derivative according to the following scheme:



Fifty grams of the acid, in convenient portions of 10 grams each, were added to an equal weight of sodium ethoxide in a capacious flask, and the mixture heated for a short time (fifteen minutes) at a temperature of about 300° in the absence of air. The dark-coloured solid thus obtained was digested with water, and the alkaline mixture extracted with ether, which removed some xylidine and a small quantity (3 grams) of a neutral oil. The alkaline liquid was next filtered from some insoluble resin, and then acidified with dilute hydrochloric acid, when a considerable quantity of acidic substance was precipitated. The mixture was extracted with ether, the ethereal solution being washed, dried, and the solvent removed. The residue thus obtained was found to contain a large proportion of unchanged 2:4-xylylsuccinamic acid, which

* Prolonged heating of this mixture causes hydrolysis, with the formation of xylidine and succinic acid.

was separated from the other acids present by treatment with cold chloroform (2:4-xylylsuccinamic acid is almost insoluble in this solvent), and filtering the mixture. The filtrate, on evaporation, yielded a residue, which slowly crystallised. The crystalline substance was separated from some oily matter by drying on a porous tile, and was then recrystallised from dilute alcohol, when colourless needles, melting at 106°, were obtained. (Found, C = 74·3; H = 7·9. $C_{11}H_{14}O_2$ requires C = 74·2; H = 7·9 per cent.)

From the analysis and properties of the above acid there can be no doubt that it is identical with β-2:4-xylylpropionic acid (compare Gattermann, *Annalen*, 1906, **347**, 347).

The neutral oil, which had been formed in the above reaction as already described, distilled at 150—200°/15 mm., and was evidently a mixture. It gave a scarlet coloration in contact with a pine shaving which had previously been moistened with concentrated hydrochloric acid, and therefore contained some compound of an indolic character. The yield of this material was, however, too small to enable it to be further investigated.

It is evident from the results of the above experiment that sodium ethoxide at a high temperature effects the disruption of 2:4-xylylsuccinamic acid with the formation of β-2:4-xylylpropionic acid, and no appreciable quantity of a substituted indole is produced.

2:4-*Xylylsuccinamide*, $C_6H_3Me_2{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}NH_2$.

This substance was prepared by the addition of concentrated aqueous ammonia to an alcoholic solution of methyl 2:4-xylylsuccinamate. In a short time the acid amide was deposited from the liquid in glistening leaflets, which melted at 203° and were pure. The compound was also obtained directly from 2:4-xylylsuccinamic acid by heating the latter for a short time with methyl alcohol containing hydrogen chloride, and then adding to the mixture an excess of concentrated aqueous ammonia, when the amide was precipitated in almost a pure condition. The yield of pure substance amounted to 80—90 per cent. of the acid employed in the reaction:

0·1503 gave 0·3598 CO_2 and 0·0987 H_2O. C = 65·3; H = 7·3.

$C_{12}H_{16}O_2N_2$ requires C = 65·5; H = 7·3 per cent.

2:4-*Xylylsuccinamide* is readily soluble in alcohol, but only sparingly so in benzene, ethyl acetate, or water. It is also soluble in concentrated hydrochloric acid, but is reprecipitated from this solution on the addition of water. When the substance is heated with aqueous potassium hydroxide, ammonia is rapidly evolved,

with the formation of 2:4-xylylsuccinamic acid, which is further resolved, on prolonged heating with the alkali, into xylidine and succinic acid.

An attempt was made to convert the above amide into an indole derivative by heating with sodium ethoxide in a manner similar to that described in connexion with 2:4-xylylsuccinamic acid, but without success, since the only compouuds that could be isolated from the reaction mixture were xylidine and 2:4-xylylsuccinamic acid.

II. *Reduction of 3-Nitro-*p*-tolylacrylic Acid* (VI, p. 1989).

The 3-nitro-*p*-tolylacrylic acid required for these experiments was prepared from *p*-tolualdehyde in the manner already described by Hanzlik and Bianchi (*Ber.*, 1899, **32**, 1288, 2285). In order to ascertain, in the first place, whether reduction could be effected by means of sodium amalgam, 800 grams of the latter (4 per cent. Na) were added in small quantities, with continuous mechanical stirring, to a solution of the acid in dilute sodium hydroxide. After the amalgam had been completely decomposed, the alkaline liquid was filtered, theu acidified, and the acidic substance, which was precipitated, was collected. The greater part of the latter was found to consist of unchanged material, but a small quantity of an indefinite acid of high melting point was isolated, which appeared to be formed from the original acid by polymerisation under the influence of the alkali. No evidence was obtained of the formation of any β-3-nitro-*p*-tolylpropionic acid (VII, p. 1989) in the reaction.

3-*Amino-*p*-tolylacrylic Acid* (VIII, p. 1990).

This compound was obtained as the first reduction product of 3-nitro-*p*-tolylacrylic acid when the latter was heated for a short time at 100° with an excess of hydriodic acid (D 1·7) and red phosphorus. As soon as the vigorous initial reaction had subsided, water was added, and the mixture filtered to remove the red phosphorus. The filtrate, on concentration, yielded well-formed crystals of a hydriodide, which were collected and dissolved in a little water. Aqueous sodium carbonate was then cautiously added to the solution, when the amino-acid was deposited as a yellow precipitate. It was purified by crystallisation from alcohol, and thus obtained in lemon-yellow, elongated needles, melting at 184°:

0·0984 gave 0·2443 CO_2 and 0·0548 H_2O. C=67·7; H=6·2.

$C_{10}H_{11}O_2N$ requires C=67·8; H=6·2 per cent.

It is evident from the above analysis that the cinnamyl residue

has remained intact during the reduction, whilst the nitro-group has been converted into an amino-group with the formation of 3-amino-*p*-tolylacrylic acid.

3-Amino-p-tolylacrylic acid is very sparingly soluble in chloroform, ether, or benzene, and moderately so in hot water or hot alcohol. It separates from the latter solvents, on cooling, in well-formed needles. It possesses both acid and basic properties, and is converted by further reduction into the following compound.

β-3-Amino-p-tolylpropionic Acid (IX, p. 1990).

This compound was prepared by heating 3-nitro-*p*-tolylacrylic acid for two hours with ten parts of hydriodic acid (D 1·7) and one part of red phosphorus. Water was then added to the reaction product, the mixture subsequently filtered, and the filtrate concentrated to a small volume, when colourless crystals of a hydriodide were deposited. These were collected, dissolved in a little water, and the free amino-acid was then precipitated by the addition of the requisite quantity of sodium carbonate. The substance was purified by crystallisation from dilute alcohol, when it was obtained in stellar aggregates of colourless needles, melting at 142—143°:

0·0952 gave 0·2340 CO_2 and 0·0650 H_2O. C=67·0; H=7·6.

$C_{10}H_{13}O_2N$ requires C=67·0; H=7·3 per cent.

β-3-Amino-p-tolylpropionic acid is readily soluble in alcohol or hot water, but only sparingly so in ether, chloroform, or benzene. Its *diacetyl* derivative, $NAc_2{\cdot}C_6H_3Me{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, prepared by heating the amino-acid with acetic anhydride for a few hours, and then pouring the mixture into water, crystallises from the latter solvent in glistening leaflets, which sinter at 122° and melt at about 160°:

0·0872 gave 0·2044 CO_2 and 0·0507 H_2O. C=63·9; H=6·5.

$C_{14}H_{17}O_4N$ requires C=63·9; H=6·5 per cent.

The *monoacetyl* derivative, $NHAc{\cdot}C_6H_3Me{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, obtained by dissolving the diacetyl compound in hot dilute (*N*/10) hydrochloric acid, and allowing the solution to cool, crystallises in colourless, slender needles, melting at 200°. It can also be prepared by heating the amino-acid, for a few minutes only, with acetic anhydride:

0·1028 gave 0·2459 CO_2 and 0·0628 H_2O. C=65·2; H=6·8.

$C_{12}H_{15}O_3N$ requires C=65·2; H=6·8 per cent.

The *ethyl* ester of *β*-3-amino-*p*-tolylpropionic acid,

$$NH_2{\cdot}C_6H_3Me{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Et,$$

prepared from the acid by treatment with hot alcohol in the

presence of hydrogen chloride, is a liquid which distils at 208°/) mm., and possesses a pleasant, nut-like odour:

0·1008 gave 0·2564 CO_2 and 0·0758 H_2O. C=69·4; H=8·4.
$C_{12}H_{17}O_2N$ requires C=69·6; H=8·2 per cent.

The above-described ester yields a *hydrochloride*,

$$CO_2Et\cdot CH_2\cdot CH_2\cdot C_6H_3Me\cdot NH_2,HCl,$$

which crystallises from a mixture of ether and alcohol in small, colourless prisms, melting at 115—117°.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

CXII.—*The Action of Chlorine on* m-*Iodoaniline and on* m-*Bromoaniline.*

By HAMILTON McCOMBIE and PERCY JAMES WARD.

THE marked influence of the presence of a hydroxyl group in the benzene nucleus on the tervalency of the iodine atom, which has been studied by Brazier and McCombie (T., 1912, **101**, 948) and by King and McCombie (this vol., p. 220), led the authors to consider the influence which other groups (especially such as possess considerable partial valency) exert on the iodine atom, and the first group which was selected for this purpose was the amino-group.

The action of chlorine on aromatic iodo-compounds which contain the amino-group seems to have been studied only very slightly. Willgerodt and Simonis (*Ber.*, 1906, **39**, 273) found that 4-iodo-*m*-toluidine (Me=1), when acted on by chlorine in chloroform solution, yielded a very unstable iododichloride, together with other higher chlorination products. Hofmann (*Annalen*, 1848, **67**, 65) noticed that p-iodoaniline with chlorine gave 2:4:6-trichloroaniline very readily. This result has been confirmed by the authors, who have found that *p*-iodoaniline does not yield an iododichloride in any solvent, even when the solution is cooled in a freezing mixture—iodine is liberated immediately. The only statement which the authors have been able to find with reference to the action of chlorine on *m*-iodoaniline is one by Willgerodt and Wikander (*Ber.*, 1907, **40**, 4068), who considered that they had obtained an unstable iododichloride. On passing chlorine into a chloroform solution of *m*-iodoaniline, these experimenters obtained a dark red powder which, they state, decomposed rapidly, yielding

a product they were unable to analyse. By treatment with sodium hydroxide, *m*-iodoaniline was regenerated, from which fact they concluded that the original substance was an iododichloride. It seems probable from our work that these chemists had in their hands merely an impure specimen of *m*-iodoaniline hydrochloride.

When a 3 per cent. solution of *m*-iodoaniline in glacial acetic acid was subjected to the action of chlorine at the ordinary temperature, a quantitative yield of 2 : 4 : 6-trichloro-3-iodoaniline was obtained. On no occasion was the formation of an iododichloride observed. If concentrated acetic acid solutions were employed, some iodine was liberated, and a considerable quantity of *m*-iodoaniline hydrochloride was deposited. When carbon tetrachloride and chloroform were employed as solvents, it was impossible to prepare much of the chlorination product, owing to the precipitation of the hydrochloride of the original iodoaniline.

The constitution of 2 : 4 : 6-trichloro-3-iodoaniline was established by heating the substance on a water-bath with excess of alcoholic ethyl nitrite and a little concentrated hydrochloric acid. By this means the amino-group was replaced by hydrogen, and there resulted 2 : 4 : 6-trichloroiodobenzene (Jackson and Gazzolo, *Amer. Chem. J.*, 1890, **22**, 52; Hantzsch, *Ber.*, 1897, **30**, 2354).

Analogous compounds to 2 : 4 : 6-trichloro-3-iodoaniline, produced by the chlorination of *m*-iodoaniline in this way, are obtained by the chlorination of the corresponding chloro- and bromo-compounds (see Beilstein and Kurbatoff, *Annalen*, 1877, **196**, 236; Orton and Reed, T., 1907, **91**, 1552).

Some interesting examples of the influence of substituents on the course of a reaction were encountered in dealing with 2 : 4 : 6-trichloro-3-iodoaniline. It was found that no hydrochloride was produced by saturating an alcoholic solution with hydrogen chloride. Benzoylation in the presence of sodium hydroxide was without effect on the compound, but in the presence of pyridine the reaction proceeded quite smoothly. In this respect the behaviour is very similar to that of the halogen substituted phenols prepared by Brazier and McCombie (*loc. cit.*). Orton and Reed (*loc. cit.*) obtained some unexpected results when acetylating 2 : 4 : 6-trichloro-3-bromoaniline. When this substance was heated with acetic anhydride for several hours, a diacetyl derivative was obtained. When, however, the acetylation was conducted by warming the compound with acetyl chloride in a sealed tube, the monoacetyl derivative was produced. Similar results have been obtained in the case of 2 : 4 : 6-trichloro-3-iodoaniline.

When *m*-iodoaniline is converted into acyl derivatives, the partial valency of the amino-group is neutralised to a certain extent, and

these acyl derivatives show tendencies for the iodine to become tervalent. In these cases iododichlorides are produced, but they prove to be very unstable. Willgerodt and Wikander (*loc. cit.*) have described the chlorination of *m*-iodoacetanilide in an ice-cold chloroform solution, and state that an iododichloride was formed, but the figures they obtained in the analysis of this compound were very high. On repeating this work, the authors have found that an iododichloride was precipitated, but that it was very unstable, and decomposed with evolution of hydrogen chloride. When chlorine was passed into a hot glacial acetic acid solution of *m*-iodoacetanilide, 2 : 4 : 6-trichloro-3-iodoacetanilide was obtained. The constitution of this compound was confirmed by its identity with the substance produced on acetylating 2 : 4 : 6-trichloro-3-iodoaniline.

Somewhat similar results were obtained in dealing with the benzoyl derivative of *m*-iodoaniline. In a cold solution an unstable iododichloride was produced, whilst in a warm solution benzoyl-2 : 4-dichloro-5-iodoaniline resulted.

If, at ordinary room temperature, chlorine is passed into an acetic acid solution of *m*-iodoaniline for several hours, the 2 : 4 : 6-trichloro-5-iodoaniline, which is at first precipitated, disappears slowly, and a clear, yellow liquid is obtained, which deposits a quantity of ammonium chloride. When the acetic acid is removed, there is obtained a crystalline substance mixed with a dark red oil. This crystalline substance, on further examination, is found to be 2 : 2 : 3 : 4 : 4 : 6-*hexachloro*-5-*iodo*-Δ^5-cyclo*hexenone*,

$$CCl_2{<}{}^{CHCl\cdot CCl_2}_{CI{=\!=}CCl}{>}CO.$$

This same compound may be obtained also by chlorinating a suspension of *m*-iodoaniline hydrochloride in acetic acid or by chlorinating *m*-iodoaniline in acetic acid at the temperature of the water bath. It is interesting to notice that in the formation of the compound the action of the chlorine has been to remove the amino-group, but the iodine atom is left untouched. Considering that in the case of *p*-iodoaniline the first action of chlorine, even in a cold solution, is to displace the iodine, it is readily seen that the position of the iodine atom in the aniline molecule is of great importance in relation to the strength of its union to the carbon atom.

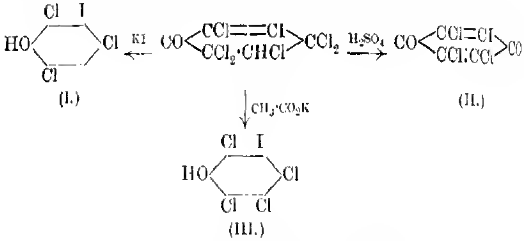
The constitution to be assigned to this ultimate chlorination product of *m*-iodoaniline is based on the following experimental facts: (1) Analyses show that there are six chlorine atoms and one iodine. As the compound is produced by the chlorination of 2 : 4 : 6-trichloro-3-iodoaniline, there must be chlorine atoms in

position 2, 4, and 6, and an iodine atom in position 3. Further, there must be one double bond in the molecule. (2) The compound, when heated with concentrated sulphuric acid on the water-bath, yielded 2 : 3 : 6-trichloro-5-iodo-*p*-benzoquinone (II). (3) The substance liberated iodine from potassium iodide, with the formation of 2 : 4 : 6-trichloro-3-iodophenol (I), and the reaction was found to proceed according to the following equation:

$$C_6HOCl_6I + 4KI = C_6HCl_3I{\cdot}OK + 3KCl + 2I_2,$$

From this reaction it follows that there must be a hydrogen atom in the molecule of the substance, and this hydrogen atom must be in the meta-position with respect to the iodine atom.

(4) 2 : 3 : 4 : 6-Tetrachloro-5-iodophenol (III) was produced by boiling the substance with potassium acetate in the presence of acetic acid. From this reaction it follows that there must be a chlorine atom in position 3, as well as a hydrogen atom. A summary of these reactions is given in the accompanying diagram:



2 : 2 : 3 : 4 : 4 : 6-Hexachloro-5-bromo-Δ^5-*cyclo*hexenone,

$$CO{<}\begin{matrix}CCl{=\!=}CBr\\ CCl_2{\cdot}CHCl\end{matrix}{>}CCl_2,$$

was obtained in exactly the same way by the chlorination of *m*-bromoaniline, and its rearrangements with the same reagents as are employed for the iodo-compound show that it is constituted similarly to that substance. Thus, this bromo-compound, when acted on by concentrated sulphuric acid, yielded 2 : 3 : 6-trichloro-5-bromo-*p*-benzoquinone; with potassium iodide there resulted 2 : 4 : 6-trichloro-3-bromophenol, and treatment with potassium acetate in presence of acetic acid resulted in the formation of 2 : 3 : 4 : 6-tetrachloro-5-bromophenol.

It is interesting to note, also, that very similar results were obtained by Zincke and Shaum (*Ber.*, 1894, **27**, 548) by the action of chlorine on *m*-chloroaniline.

These chemists obtained two products in this reaction, namely, 2 : 3 : 4 : 4 : 5 : 6 : 6-heptachloro-Δ^2-*cyclo*hexenone and 2 : 2 : 3 : 4 : 5 : 6 : 6-heptachloro-Δ^3-*cyclo*hexenone.

Experimental.

The *m*-iodoaniline used in these experiments was prepared from *m*-nitroaniline according to the method described by Baeyer (*Ber.*, 1905, **38**, 2761), but this method was modified in the second stage of the reaction, namely, the conversion of the *m*-iodonitrobenzene into *m*-iodoaniline. This reduction was effected by Baeyer in the presence of methylated spirit, and it was found that after neutralisation and steam distillation, considerable quantities of *m*-iodoaniline were dissolved in the methylated spirit, and could not be recovered by dilution with water. Our modification consisted in distilling off the methylated spirit before neutralising the solution.

m-*Iodoaniline Hydrochloride*, $C_6H_4I \cdot NH_2,HCl$.

This compound was prepared by passing a stream of dry hydrogen chloride into a solution of *m*-iodoaniline in ethyl alcohol. Most of the solvent was then allowed to evaporate, and the hydrochloride was obtained in large, white leaflets, which melted at 260°:

0·1000 gave 0·1488 AgCl + AgI.

C_6H_6NI,HCl requires AgCl + AgI = 0·1481.

A suspension of *m*-iodoaniline hydrochloride in glacial acetic acid was chlorinated for about an hour. The hydrochloride gradually disappeared, hydrogen chloride was evolved, and the solution was found to contain 2 : 3 : 3 : 4 : 4 : 6-hexachloro-5-iodo-Δ^5-*cyclo*hexenone, melting at 104°.

Action of Chlorine on m-*Iodoacetanilide: Preparation of 2:4:6-Trichloro-3-iodoacetanilide.*

m-Iodoacetanilide, which was prepared by heating *m*-iodoaniline with acetic anhydride and a drop of acetyl chloride, was dissolved in glacial acetic acid, and the solution heated to the boiling point. A stream of chlorine was passed through the solution, and, when the evolution of hydrogen chloride had ceased, the liquid was concentrated to a small bulk. The white crystals which appeared were separated and recrystallised from a mixture of acetic acid and water, when they consisted of short needles, melting at 204°:

0·0941 gave 0·1715 AgCl + AgI.

$C_8H_5ONCl_3I$ requires AgCl + AgI = 0·1718.

2 : 4 : 6-*Trichloro-3-iodoacetanilide* is moderately soluble in acetic acid or light petroleum, very soluble in ethyl alcohol, and only sparingly so in acetone.

Benzoyl-m-*iodoaniline*, $C_6H_4I\cdot NHBz$.

This compound was prepared by benzoylation in presence of sodium hydroxide. When recrystallised twice from methylated spirit, it separated in slender, white needles, melting at 156—157°:

0·1000 gave 0·0719 AgI. I=38·85.

$C_{13}H_{10}ONI$ requires I=39·32 per cent.

Action of Chlorine on Benzoyl-m-*iodoaniline: Preparation of Benzoyl*-2:4-*dichloro*-5-*iodoaniline*.

On passing chlorine into a solution of benzoyl-*m*-iodoaniline in glacial acetic acid, an unstable iododichloride was at first precipitated. On boiling the solution, this unstable compound dissolved, and the passage of chlorine through the hot solution was continued. The solution was concentrated, and the short, white needles which appeared were separated and recrystallised from a mixture of glacial acetic acid and water, when the product was found to melt at 142°:

0·0708 gave 0·0932 AgCl + AgI.

$C_{13}H_8ONCl_2I$ requires AgCl + AgI = 0·0943.

Action of Chlorine on m-*Iodoaniline: Preparation of* 2:4:6-*Trichloro*-3-*iodoaniline*.

Ten grams of powdered *m*-iodoaniline were dissolved in 350 c.c. of glacial acetic acid, and a stream of chlorine was led into the solution. After a few minutes the liquid became dark green, then the colour changed to pale yellow, and fine, white crystals began to separate, accompanied by a rapid evolution of hydrogen chloride. The solution was then cooled, and the contents of the beaker were found to be almost solid. The crystals were separated, and the liquid subjected to the further action of chlorine, which process was continued until no more solid separated. The crude solid was washed with dilute sodium carbonate solution, and was found to weigh 12—13 grams. It was recrystallised from methyl alcohol, and separated in short, slender needles, melting at 88°:

0·1380 gave 0·2837 AgCl + AgI.

$C_6H_3NCl_3I$ requires AgCl + AgI = 0·2847.

2:4:6-*Trichloro*-3-*iodoaniline* is sparingly soluble in acetic acid, methyl alcohol, or light petroleum, and readily so in ethyl alcohol or acetone. The crystals assume a pink tinge after being kept for a short period. When subjected to the action of chlorine for a long time at the ordinary temperature or a shorter time

at the temperature of the water-bath, this compound yields 2 : 2 : 3 : 4 : 4 : 6-hexachloro-5-iodo-Δ^5-*cyclo*hexenone. 2 : 4 : 6-Trichloro-3-iodoaniline was boiled on the water-bath with an excess of alcoholic ethyl nitrite and a little concentrated hydrochloric acid; the alcohol was distilled off, and the residue was recrystallised from a mixture of glacial acetic acid and water, when a compound melting at 55° was obtained. This substance proved to be 2 : 4 : 6-trichloroiodobenzene, previously described by Jackson and Gazzolo (*loc. cit.*) and by Hantzsch (*loc. cit.*). This reaction establishes the constitution of this chlorination product of *m*-iodoaniline.

Benzoyl-2 : 4 : 6-*trichloro-3-iodoaniline.*

It was found that 2 : 4 : 6-trichloro-3-iodoaniline could not be converted into the benzoyl derivative by the action of benzoyl chloride in the presence of sodium hydroxide, so that recourse was had to the pyridine method of benzoylation.

One gram of 2 : 4 : 6-trichloro-3-iodoaniline was dissolved in pyridine, and 0·5 gram of pure benzoyl chloride was added carefully. The solution was allowed to remain overnight, and was then poured into dilute hydrochloric acid. After several hours the precipitated product solidified, and, after separation, was washed with warm methyl alcohol, in which it is only sparingly soluble; after three recrystallisations from ethyl alcohol the benzoyl derivative was obtained in glistening, white leaflets, which melted at 229°:

0·0910 gave 0·1408 AgCl + AgI.

$C_{13}H_7ONCl_3I$ requires AgCl + AgI = 0·1420.

Benzoyl-2 : 4 : 6-*trichloro-3-iodoaniline* is only sparingly soluble in acetone, but is moderately so in acetic acid; it is quite insoluble in benzene.

Preparation of 2 : 4 : 6-*Trichloro-3-iodoacetanilide from* 2 : 4 : 6-*Trichloro-3-iodoaniline.*

This compound was prepared by heating 2 : 4 : 6-trichloro-3-iodoaniline with an excess of acetyl chloride in a sealed tube on the water-bath. After being heated for fifteen minutes the tube was opened, the excess of acetyl chloride removed in a current of air, and the residue when recrystallised from a mixture of acetic acid and water proved identical with the product obtained by the chlorination of *m*-iodoacetanilide.

Chlorination of a Hot Solution of m-*Iodoaniline: Preparation of* 2 : 2 : 3 : 4 : 4 : 6-*Hexachloro*-5-*iodo*-Δ^5-cyclo*hexenone*.

Ten grams of *m*-iodoaniline were dissolved in 350 c.c. of glacial acetic acid, the solution was warmed for a few minutes on a water-bath, and a stream of chlorine was passed through the solution. After a short time hydrogen chloride was evolved readily, and white crystals of ammonium chloride were deposited. When the chlorination had proceeded for about two hours, the evolution of hydrogen chloride had practically ceased, and the solution was then evaporated to dryness. The residue was washed with water to remove the ammonium chloride produced in the reaction, and there resulted about 18 grams of a crude oily product, with an odour strongly resembling that of camphor. This product, when re-crystallised from glacial acetic acid, separated in large, transparent prisms, which melted at 104°:

0·1023 gave 0·2631 AgCl + AgI.

C_6HOCl_6I requires AgCl + AgI = 0·2614.

2 : 2 : 3 : 4 : 4 : 6-*Hexachloro*-5-*iodo*-Δ^5-cyclo*hexenone* is moderately soluble in methyl and ethyl alcohols, sparingly so in glacial acetic acid, and very soluble in acetone.

The method of preparation described above was not always satisfactory. In some cases the reaction proceeded too vigorously, resulting in the liberation of a large amount of iodine, probably producing a fair quantity of 2 : 3 : 4 : 4 : 5 : 6 : 6-heptachloro-Δ^2-*cyclo*hexenone, from which it is a matter of great difficulty to separate the iodo-compound.

If the chlorination was conducted in a cold solution, no iodine was liberated. Under these conditions the reaction required two days for completion, and a considerable quantity of the oily by-product was obtained.

When this compound was treated with concentrated sulphuric acid, it yielded trichloroiodobenzoquinone; with potassium iodide, it yielded trichloroiodophenol; and with potassium acetate, tetra-chloroiodophenol. These reactions established its constitution.

2 : 4 : 6-*Trichloro*-3-*iodophenol*.

Five grams of 2 : 2 : 3 : 4 : 4 : 6-hexachloro-5-iodo-Δ^5-*cyclo*hexenone were dissolved in warm glacial acetic acid, and 10 grams of powdered potassium iodide were added. Liberation of iodine commenced immediately, and when the mixture had been warmed on the water-bath for half an hour, the reaction was complete. The iodine was removed by the addition of sodium hydrogen

sulphite, and the phenol was separated and recrystallised from a mixture of glacial acetic acid and water. It crystallised in white, silky needles, melting at 102°:

0·0879 gave 0·1826 AgCl + AgI.

$C_6H_2OCl_3I$ requires AgCl + AgI = 0·1808.

2 : 4 : 6-*Trichloro-3-iodophenol* is moderately soluble in ethyl and methyl alcohols, and readily so in acetic acid.

The *acetyl* derivative, $C_6H_2Cl_3I{\cdot}OAc$, was prepared by the action of acetic anhydride on 2 : 4 : 6-trichloro-3-iodophenol. It crystallises from a concentrated alcoholic solution in small leaflets, melting at 87°:

0·0555 gave 0·1034 AgCl + AgI.

$C_8H_4O_2Cl_3I$ requires AgCl + AgI = 0·1010.

The *benzoyl* derivative, $C_6H_2Cl_3I{\cdot}OBz$, was prepared by the pyridine method, and when recrystallised from ethyl alcohol separated in small needles, which melted at 136—138°:

0·0620 gave 0·0967 AgCl + AgI.

$C_{13}H_6O_2Cl_3I$ requires AgCl + AgI = 0·0965.

This derivative is readily soluble in acetone, and sparingly so in ethyl and methyl alcohols.

2 : 3 : 6-*Trichloro-5-iodo-p-benzoquinone.*

This compound was prepared by heating hexachloroiodo*cyclo*hexenone cautiously with concentrated sulphuric acid on a water-bath for about four hours. The solution was poured into water; the product, after separation, was washed first with water, and then with methyl alcohol:

0·0460 gave 0·0920 AgCl + AgI.

$C_6O_2Cl_3I$ requires AgCl + AgI = 0·0907.

2 : 3 : 6-*Trichloro-5-iodo-p-benzoquinone* possesses a deep reddish-yellow colour, and can be sublimed at about 150°; it melts indefinitely at about 280°. When attempts were made to recrystallise it from methyl alcohol it was found that decomposition took place. In other organic solvents it was practically insoluble.

2 : 3 : 4 : 6-*Tetrachloro-5-iodophenol.*

Four grams (1 mol.) of hexachloroiodo*cyclo*hexenone were heated on the water-bath with three grams (3 mols.) of potassium acetate in the presence of acetic acid. After two hours the mixture was poured into water, the phenol was separated, and the residue washed well with water, and then recrystallised three times from

light petroleum, in which it is only sparingly soluble. It was obtained in long, white needles, melting at 169°:

0·0596 gave 0·1359 AgCl + AgI.

C_6HOCl_4I requires AgCl + AgI = 0·1347.

2 : 3 : 4 : 6-*Tetrachloro-5-iodophenol* is moderately soluble in acetic acid, and also in methyl and ethyl alcohols.

The *acetyl* derivative, $C_6HCl_4I{\cdot}OAc$, was prepared by heating tetrachloroiodophenol with acetic anhydride. It was crystallised from ethyl alcohol, from which it separated in glistening, short needles, melting at 140—141°:

0·0477 gave 0·0967 AgCl + AgI.

$C_8H_3O_2Cl_4I$ requires AgCl + AgI = 0·0964.

The acetyl derivative is sparingly soluble in ethyl alcohol, and moderately so in methyl alcohol.

The *benzoyl* derivative, $C_6HCl_4I{\cdot}OBz$, was prepared by the pyridine method, and when recrystallised from ethyl alcohol separated in small, white prisms, melting at 175—176°:

0·0609 gave 0·1060 AgCl + AgI.

$C_{13}H_5O_2Cl_4I$ requires AgCl + AgI = 0·1066.

This compound is only sparingly soluble in methyl and ethyl alcohols, insoluble in light petroleum, and readily soluble in acetone.

Chlorination of a Hot Solution of m-*Bromoaniline: Preparation of* 2 : 2 : 3 : 4 : 4 : 6-*Hexachloro-5-bromo-Δ^5-*cyclo*hexenone.*

$$CO{<}\begin{matrix}CCl{=}CBr\\CCl_2{\cdot}CHCl\end{matrix}{>}CCl_2.$$

This compound was prepared in a manner similar to that employed for the corresponding iodo-compound. When crystallised from glacial acetic acid, it forms transparent prisms, melting at 106°:

0·0923 gave 0·2558 AgCl + AgBr.

C_6HOCl_6Br requires AgCl + AgBr = 0·2534.

The solubilities of this bromo-compound were of the same order as those of the iodo-compound, thus, it is moderately soluble in methyl and ethyl alcohols, and sparingly so in glacial acetic acid.

2 : 4 : 6-*Trichloro-3-bromophenol.*

Two grams of hexachlorobromo*cyclo*hexenone were treated with 6 grams of powdered potassium iodide in the presence of acetic acid by the method used for the preparation of trichloroiodophenol. The product was crystallised from a mixture of acetic acid and

water, from which it separated in white, silky needles, melting at 61°:

0·0936 gave 0·2115 AgCl + AgBr.

$C_6H_2OCl_3Br$ requires AgCl + AgBr = 0·2095.

2 : 4 : 6-*Trichloro-3-bromophenol* is moderately soluble in methyl and ethyl alcohols and in glacial acetic acid.

The *acetyl* derivative, $C_6HCl_3Br{\cdot}OAc$, was obtained by the action of acetic anhydride and crystallised in small leaflets, melting at 70°:

0·0644 gave 0·1266 AgCl + AgBr.

$C_8H_4O_2Cl_3Br$ requires AgCl + AgBr = 0·1252.

The *benzoyl* derivative, $C_6HCl_3Br{\cdot}OBz$, was prepared in pyridine solution, and when recrystallised from ethyl alcohol melted at 102°:

0·0447 gave 0·0732 AgCl + AgBr.

$C_{13}H_6O_2Cl_3Br$ requires AgCl + AgBr = 0·0727.

2 : 3 : 6-*Trichloro-5-bromo-p-benzoquinone.*

This was prepared by heating hexachlorobromo*cyclo*hexenone with concentrated sulphuric acid for three hours on a water-bath. The acid liquid was poured into water, and the yellow product was crystallised from much methyl alcohol, in which it is only sparingly soluble. It was obtained in bright yellow leaflets, melting at 292° (Found, AgCl + AgBr = 0·1798. Calculated, 0·1774). This substance has been described by several investigators, notably by Levy and Schultz (*Annalen*, 1881, **210**, 162), who prepared it by the action of bromine on trichlorobenzoquinone.

2 : 3 : 4 : 6-*Tetrachloro-5-bromophenol.*

Hexachlorobromo*cyclo*hexenone (1 mol.), dissolved in acetic acid, was treated with potassium acetate (3 mols.) in a manner similar to that employed in the case of the corresponding iodo-compound. It was crystallised from light petroleum, when it separated in white needles, melting at 192°:

0·0531 gave 0·1324 AgCl + AgBr.

C_6HOCl_4Br requires AgCl + AgBr = 0·1300.

The *acetyl* derivative, $C_6Cl_4Br{\cdot}OAc$, was obtained by means of acetic anhydride, and when crystallised from ethyl alcohol yielded slender, glistening needles, melting at 144°:

0·0610 gave 0·1334 AgCl + AgBr.

$C_8H_3O_2Cl_4Br$ requires AgCl + AgBr = 0·1317.

This substance is only sparingly soluble in ethyl and methyl alcohols, but is readily soluble in acetone.

The *benzoyl* derivative, $C_6Cl_4Br{\cdot}OBz$, was prepared in pyridine

solution, and crystallised from methyl alcohol in small, white prisms, melting at 169°:

0·0505 gave 0·0921 $AgCl+AgBr$.

$C_{13}H_5O_2Cl_4Br$ requires $AgCl+AgBr=0·0927$.

This substance is sparingly soluble in methyl and ethyl alcohols, but dissolves readily in acetone.

CHEMICAL DEPARTMENT,
THE UNIVERSITY, EDGBASTON,
BIRMINGHAM.

CCXIII.—*The Constituents of Senna Leaves.*

By FRANK TUTIN.

SENNA leaves have in the past been the subject of numerous investigations, but until recently little information has been obtained regarding the definite compounds present in them. Most of the investigators have recorded the isolation of "chrysophanic acid" and the "cathartic acid" of Dragendorff—a product to which the purgative action of the drug has been attributed—but which for some time has been recognised as an indefinite mixture of substances.

The most recent investigation of importance on this subject is that by Tschirch and Hiepe (*Arch. Pharm.*, 1900, **238**, 427), where a detailed mention of the previous literature will be found. These investigators described the isolation of the following products: A crystalline substance, $C_{14}H_{10}O_5$; "sennarhamnetin"; "anthraglucosennin"; "senna-emodin"; "sennachrysophanic acid"; "senna*iso*emodin," and amorphous "sennanigrin." No melting point was recorded for the "substance, $C_{14}H_{10}O_5$," and in view of the results of the present investigation it would appear probable that it was a mixture of aloe-emodin and rhein. The latter substance, which has now been isolated from senna, had previously been known to occur only in rhubarb. With regard to the "sennarhamnetin," Tschirch and Hiepe record no analysis, and merely state that the product in question did not melt at 260°. It is now shown, however, that the flavone product present in various specimens of senna leaves consists either of kaempferol (m. p. 274°) or of a mixture of the latter with *iso*rhamnetin (m. p. 302°). The "anthraglucosennin" of the last-mentioned authors would appear to have been a mixture of the glucosides of rhein

nd aloe-emodin, the latter compound being the so-called "senna-nodin." "Sennanigrin" is an amorphous, indefinite product, and ie occurrence of "sennachrysophanic acid" (chrysophanol) and of sennaisoemodin"—for which no melting point is given—cannot e confirmed.

With regard to the alleged occurrence of chrysophanic acid in enna, it is stated by Tschirch and Hiepe (*loc. cit.*, p. 435) that he product obtained by them was free from methoxyl, and melted t 171—172°. In subsequent communications, however (Tschirch nd Bromberger, *Arch. Pharm.*, 1911, **249**, 222, and Tschirch and Veil, *ibid.*, 1912, **250**, 26), it is emphasised that pure methoxyl-ree chrysophanic acid (chrysophanol) melts at 196°. Notwith-tanding these differences of melting point, in the former of these papers (*loc. cit.*) it is stated that senna was the first drug in which pure chrysophanol had been observed to occur. It may therefore be noted that the three varieties of senna leaves which have now been examined were found to be devoid of chrysophanol, the only anthraquinone derivatives present being rhein and aloe-emodin.

A summary of the results of the present investigation will be found at the end of this paper.

Experimental.

I. *Tinnevelly Senna Leaves.*

The material employed for this investigation consisted of the best quality of Tinnevelly senna leaves.

A small portion (10 grams) of the ground material was treated with Prollius' fluid, and the resulting extract tested for an alkaloid with the usual reagents, but with a negative result.

Another portion (20 grams) of the ground leaves was succes-sively extracted in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried at 100°, were obtained:

Petroleum (b. p. 35—50°)	extracted	0·89 gram	=	4·45 per cent.
Ether	,,	0·25 ,,		1·25 ,,
Chloroform	,,	0·22 ,,		1·10 ,,
Ethyl acetate	,,	1·30 ,,		6·50 ,,
Alcohol	,,	3·18 ,,		15·90 ,,
	Total =	5·84 grams	=	29·20 per cent.

For the purpose of a complete examination of the constituents of the leaves, 22·54 kilograms of the dried, ground material were extracted by continuous percolation with hot alcohol. After the removal of the greater part of the solvent, 11·5 kilograms of a viscid, dark green extract were obtained.

Two kilograms of the above-mentioned extract were mixed with

water and distilled in a current of steam, when a quantity (1·5 grams) of a dark-coloured essential oil was obtained, which possessed a strong aromatic odour. There then remained in the distillation flask a dark-coloured aqueous liquid (*A*) and a quantity of a soft, dark green resin (*B*). These products were separated when cold, and the resin washed several times with aqueous ammonium sulphate, the washings being kept separate from the main bulk of the aqueous liquid. This procedure was necessitated by the fact that the resin formed an inseparable emulsion on attempting to wash it with water.

Examination of the Aqueous Liquid (A).

The aqueous liquid, after concentration under diminished pressure, was extracted many times with ether. These ethereal liquids were united, the greater part of the solvent removed, and the residue largely diluted with light petroleum (b. p. 35—50°), when the greater part of the dissolved material was precipitated as a brown solid. On decanting and concentrating the supernatant liquid, and again treating it with light petroleum, further small quantities of a similar solid were obtained, which were added to the first portion. The petroleum liquid was finally evaporated, the residue dissolved in ether, and the ethereal solution shaken successively with aqueous ammonium carbonate, sodium carbonate, and potassium hydroxide.

The ammonium carbonate extract was acidified, and extracted with ether, when a yellow, viscid product was obtained. The latter was digested with warm water and treated with animal charcoal, when the filtrate yielded a small amount of an acid, which separated in colourless needles, melting at 155°, and was identified as salicylic acid.

The sodium carbonate extract yielded only an amorphous, brown powder, but on acidifying the liquid obtained by means of aqueous potassium hydroxide a product was obtained, which was found to consist largely of aloe-emodin. This substance was subsequently obtained in larger amount, and its isolation will be described later.

Isolation of Rhein, $C_{14}H_5O_2(OH)_2\cdot CO_2H$.

The above-mentioned brown solid which had been precipitated by means of light petroleum was digested with a considerable volume of ether, when a quantity (about 0·5 gram) of a yellowish-brown powder remained undissolved. The latter was collected, and dissolved in pyridine, from which it separated in orange-coloured needles, melting at about 318°. (Found, C = 63·2; H = 2·9. $C_{15}H_8O_6$ requires C = 63·4; H = 2·8 per cent.)

This substance is thus seen to be rhein (4:5-dihydroxyanthraquinone-2-carboxylic acid), a substance which has previously been isolated only from rhubarb. On acetylation it gave diacetylrhein, which separated from acetic anhydride in yellow needles containing solvent of crystallisation, and, after drying at 130°, melted at 258°. The apparently anomalous behaviour which had previously been observed to occur on heating diacetylrhein with xylene (T., 1911, **99**, 952) was found to be due to the loss of acetic anhydride of crystallisation.

The ethereal solution from which the crude rhein had been separated, as above described, was shaken with concentrated aqueous ammonium carbonate, when a yellowish-brown precipitate was produced. The latter was collected, and the aqueous and ethereal layers then separated, when, on acidifying the former, it yielded only a small amount of amorphous, brown material. The above-mentioned precipitate, however, proved to be the ammonium salt of rhein, which, although readily soluble in water, is practically insoluble in concentrated aqueous ammonium carbonate. It yielded rhein, melting at about 318—320°.

Isolation of Kaempferol, $C_{15}H_6O_2(OH)_4$.

The ethereal liquid which had been extracted with aqueous ammonium carbonate, as above described, was shaken with successive portions of dilute aqueous sodium carbonate until the resulting aqueous liquids, the first of which were deep yellow, commenced to acquire a red tint. Each of the alkaline liquids was acidified as soon as it was separated from the ether, and the precipitated solid then collected. On examination, the latter proved to be a mixture of a flavone derivative with some aloe-emodin, and the complete separation of these two substances was found to be possible only by re-dissolving the mixture in ether, and repeating the above-described fractional extraction with dilute aqueous sodium carbonate two or three times, when the aloe-emodin was eventually all left behind in the ether. The flavone derivative, when freed from aloe-emodin, was crystallised by concentrating its solution in slightly diluted alcohol, when it formed small, bright yellow needles, melting at 274°, and this melting point was not altered by further crystallisation. (Found, C = 62·9; H = 3·8. $C_{15}H_{10}O_6$ requires C = 62·9; H = 3·5 per cent.)

The above-described substance, which gave a yellow colour on treatment with alkalis, and dissolved in concentrated sulphuric acid yielding a liquid possessing a strong, blue fluorescence, was identified as kaempferol (1:3:4-trihydroxyflavonol). On acetylation it yielded tetra-acetylkaempferol, which, when crystallised with

ether, ethyl acetate, or alcohol, formed colourless needles, which had a dual melting point, as observed by A. G. Perkin (T., 1902, 81, 587); thus, fusion first occurs at about 119—120°, the product then gradually resolidifies, and subsequently melts at 183°. (Found C=60·3; H=4·1. $C_{23}H_{18}O_{10}$ requires C=60·7; H=4·0 per cent.)

The statement made by Perkin that the dual melting point of tetra-acetylkaempferol is not due to the presence of solvent of crystallisation cannot, however, be confirmed. Specimens crystallised from each of the solvents mentioned, when carefully heated for several hours at 110°, suffered a diminution in weight without undergoing any softening, and then melted sharply at 183°; for example, an air-dried specimen which had been crystallised from ethyl acetate, on drying at 110°, gave the following results:

0·1124 lost 0·0085 of solvent. $C_4H_8O_2$=8·6.

$C_{23}H_{18}O_{10},\frac{1}{2}C_4H_8O_2$ requires $C_4H_8O_2$=8·8 per cent.

Tetrabenzoylkaempferol.—No benzoyl derivative of kaempferol appears heretofore to have been described. Kaempferol was benzoylated in pyridine solution, the mixture diluted with water, and the precipitated *tetrabenzoylkaempferol* collected. It was very sparingly soluble in most of the usual organic solvents, but separated in tufts of small, colourless needles when its solution in hot xylene was diluted with ethyl acetate. It had a dual melting point, similar to that of the corresponding acetyl derivative, and, in this case also, this behaviour was due to the presence of solvent of crystallisation. Tetrabenzoylkaempferol, after drying at 130°, melts at 205°, then gradually resolidifies, after which it melts at 237—238°. After drying for five hours at 170° it melts at 237—238°, without previous softening:

0·1052 * gave 0·2824 CO_2 and 0·0363 H_2O. C=73·2; H=3·8.

$C_{43}H_{26}O_{10}$ requires C=73·5; H=3·7 per cent.

No further compound could be isolated from the mother liquors from the above-described kaempferol, but in view of the statement of Tschirch and Hiepe (*Arch. Pharm.*, 1900, **238**, 439) that senna leaves contain "sennarhamnetin," it was deemed desirable further to investigate this point. An additional amount of extract was therefore worked up, and the crude flavone derivative obtained from it was submitted to the action of hydriodic acid in a Zeisel apparatus, but no methyl iodide was evolved. It is thus evident that no rhamnetin, which is a monomethyl ether of quercetin, was present in the Tinnevelly senna leaves. Moreover, another sample of the same variety of leaves yielded a similar product consisting solely of kaempferol.

* Dried at 170°.

Isolation of Aloe-emodin, $C_{14}H_5O_2(OH)_2\cdot CH_2\cdot OH$.

The ethereal liquid from which the kaempferol had been removed, above described, contained a substance which was somewhat ly extracted by fairly concentrated aqueous sodium carbonate, t quickly removed by dilute potassium hydroxide. It was erefore extracted by means of the latter alkali, after which the her was found to contain only a small amount of amorphous, utral material. On acidifying the red, alkaline extracts, a ownish-yellow substance was precipitated, which was collected on filter. This material was crystallised from ethyl acetate, when yielded long, lustrous needles of a brownish-orange colour, which elted at about 218°, and proved to be aloe-emodin. (Found, =66·5; H=3·8. Calc., C=66·7; H=3·7 per cent.) It was mpared with aloe-emodin obtained from aloes and from rhubarb, d found to be identical with both these preparations. It yielded iacetylaloe-emodin, which formed pale yellow needles, melting at 4—174·5°, and tribenzoylaloe-emodin, melting at 232°. In view the statement of Tschirch and Hiepe (*loc. cit.*, p. 435) that senna aves contain "sennachrysophanic acid," the mother liquors from e aloe-emodin were carefully investigated for the presence of rysophanol ("chrysophanic acid"), but with a negative result.

The aqueous liquid from which the above-described compounds ad been removed by extraction with ether, as previously menoned, was acidified with dilute sulphuric acid, when a darkloured, amorphous precipitate separated, and was collected. The tter consisted chiefly of resinous material, but it also contained me rhein, which had doubtless been present in the aqueous quid in the form of a salt. The aqueous liquid, which, after this eatment, was much lighter in colour, was deprived of sulphuric cid by the cautious addition of barium hydroxide, filtered, and en extracted many times with amyl alcohol. The resulting xtracts, when washed, and concentrated under diminished pressure a small bulk, deposited, on cooling, a quantity of a brown, morphous solid, which was collected. The filtrate from this solid ielded, on evaporation, a smaller amount of a viscid, amorphous roduct, but it did not appear to contain any tannin, and nothing rystalline could be directly isolated from it. A portion of it was issolved in water, and heated with dilute sulphuric acid for some ime. This resulted in the formation of some brown, resinous aterial, together with dextrose, but no other definite substance ould be isolated. Some amorphous, glucosidic material was therefore present.

The remaining portion of the material readily soluble in cold amyl alcohol was boiled for a minute with dilute aqueous potassium hydroxide, after which it was acidified and extracted with ether. There were then obtained, in addition to brown, amorphous products, small amounts of kaempferol and aloe-emodin.

Isolation of a New Glucoside, Kaempferin, $C_{27}H_{30}O_{16},6H_2O$.

The material which had separated on concentrating the amyl alcohol solution, as above described, was deprived of the latter solvent, dissolved in boiling alcohol, and treated with animal charcoal, when, on cooling the filtrate, yellowish-brown, somewhat gelatinous granules separated. A little water was then added, and the mixture kept in a flask for some five months, alcohol being added from time to time to compensate for the loss by evaporation. At the end of this time yellow crystals commenced to form, and gradually spread throughout the liquid, the granular material at the same time passing into solution. The crystalline solid was then collected, and recrystallised from water, when it quickly separated in yellow needles, which melted and decomposed at 185—195°. This substance had the properties of a glucoside, since, when heated with dilute sulphuric acid, it yielded kaempferol (m. p. 274°) and dextrose. The latter gave *d*-phenylglucosazone, melting at 212°. No glucoside of kaempferol agreeing in properties with the one here described has previously been known, and the name *kaempferin* is therefore proposed for the new compound:

0·1741,* on heating at 155°, lost 0·0277 H_2O. $H_2O=15·8$.

0·1454 † gave 0·2804 CO_2 and 0·0655 H_2O. C=52·8; H=5·0.

$C_{27}H_{30}O_{16},6H_2O$ requires $H_2O=15·0$ per cent.

$C_{27}H_{30}O_{16}$ requires C=53·1; H=4·9 per cent.

0·1039 ‡ gave 0·1978 CO_2 and 0·0492 H_2O. C=51·9; H=5·2.

$C_{27}H_{30}O_{16},H_2O$ requires C=51·6; H=5·1 per cent.

It thus appears from the above analytical results that kaempferin yields two molecules of dextrose on hydrolysis. It crystallises from water with 6 molecules of the latter, 5 of which are eliminated at 130° and the remaining one at a higher temperature. *Acetyl-* and *benzoyl-kaempferin* were prepared, but both were found to be uncrystallisable.

The original aqueous alcoholic filtrate from the crude kaempferin could not be caused to deposit any further crystalline substance, although it contained a considerable amount of material. With

* Dried in the air for fourteen hours.

† Dried at 155°.

‡ Dried until constant at 130°.

the exception of the uncrystallisable nature of the latter, its properties indicated it to be a mixture of glucosides of anthraquinone derivatives similar to that occurring in rhubarb (T., 1911, **99**, 957). It was therefore hydrolysed by heating for some time with 2·5 per cent. aqueous sulphuric acid, after which the mixture was extracted several times with ether. The resulting ethereal liquid was then examined in a manner similar to that indicated in connexion with the ether extract of the aqueous liquid, when considerable amounts of rhein and aloe-emodin were obtained, together with a little kaempferol. No chrysophanol was present. The acid aqueous liquid, from which these substances had been removed by means of ether, was deprived of sulphuric acid by treatment with barium hydroxide, when the filtered liquid was found to contain an abundance of sugar. It readily yielded *d*-phenylglucosazone, melting at 212°.

It is evident, therefore, that senna leaves contain, in addition to the new glucoside, kaempferin, a quantity of the glucosides of rhein and aloe-emodin, but, as was ascertained in connexion with the investigation of rhubarb (*loc. cit.*), these substances are devoid of purgative action.

The aqueous liquid which had been extracted with amyl alcohol was freed from the latter solvent, concentrated to a small bulk, and then largely diluted with alcohol. On keeping the mixture it deposited a considerable amount of a crystalline solid, mixed with a dark brown, syrupy product. The solid was collected, and separated so far as possible from the syrup, after which it was found possible to obtain it in a colourless condition by repeated crystallisation from dilute alcohol. This product was found to be a mixture of the sodium, potassium, and magnesium salts of an organic acid, the magnesium salt preponderating. It was fractionally crystallised many times from dilute alcohol, but no separation could be effected. No sparingly soluble salt or crystalline derivative of the acid could be prepared, nor could the acid be isolated except in the form of a gummy mass. It was impossible, therefore, to identify it.

Some of the earlier investigators have recorded the presence in senna of calcium malate and tartrate, but the above-described mixture of salts contained neither of these substances.

The original aqueous-alcoholic liquid which had been decanted from the crude mixture of salts, together with the syrupy material separated from the latter, was deprived of alcohol, diluted with water, and then treated with a slight excess of aqueous basic lead acetate. The yellow precipitate thus formed was collected, and

washed, after which it was suspended in water and decomposed by means of hydrogen sulphide. On concentrating the filtered liquid a brown, viscid product was obtained, from which nothing crystalline could be directly separated. It was therefore boiled for a minute with dilute aqueous potassium hydroxide, acidified, and extracted with ether. There were thus obtained, in addition to dark brown, amorphous products, a little rhein, a considerable amount of kaempferol, and a moderate quantity of aloe-emodin.

The filtrate from the basic lead acetate precipitate was deprived of lead by means of hydrogen sulphide, filtered, and concentrated under diminished pressure to the consistency of a syrup. This material deposited nothing on keeping, but it evidently contained a large amount of sugar, since it readily yielded *d*-phenylglucosazone, melting at 215°.

Examination of the Resin (B).

The resin (*B*), which formed a dark green, viscid mass, amounted to about 290 grams, being thus equivalent to about 7·0 per cent. of the weight of the leaves employed. It was mixed with purified sawdust, and the dried mixture thoroughly extracted in a large Soxhlet apparatus with petroleum (b. p. 35—50°), ether, chloroform, ethyl acetate, and alcohol.

Petroleum Extract of the Resin.

This extract of the resin, after complete removal of the solvent, formed a dark green, oily mass, and amounted to 241 grams. It was digested with a large volume of ether, and the mixture cooled and filtered. A quantity (about 3 grams) of a green, sparingly soluble solid was thus obtained, which, after being twice distilled under diminished pressure, and crystallised several times from ethyl acetate, proved to be myricyl alcohol, a larger amount of which was subsequently isolated.

The ethereal solution from which the crude myricyl alcohol had been removed was washed with water, when a dark-coloured, aqueous liquid was obtained. The latter was found to consist of a colloidal solution of a resin, and on treatment with an aqueous solution of an inorganic salt or mineral acid it yielded a dark, resinous precipitate. Nothing definite, however, could be isolated from the latter. The washed ethereal liquid was then shaken successively with aqueous ammonium carbonate, potassium carbonate, and potassium hydroxide. Much difficulty was experienced in separating the resulting aqueous liquids owing to the formation of emulsions, which were found to be caused by the separation

of further amounts of myricyl alcohol, contaminated with much chlorophyll. The dark-coloured alkaline liquid obtained by extraction with ammonium carbonate was acidified, re-extracted with ether, and the ethereal solution fractionally extracted with aqueous ammonium carbonate. Rhein was then obtained, together with some dark-coloured, amorphous products. The alkaline liquid obtained by means of aqueous potassium carbonate, when treated in an analogous manner, yielded chiefly amorphous products, together with small amounts of kaempferol and aloe-emodin, whilst the potassium hydroxide extract yielded considerable amounts of the last-mentioned anthraquinone derivative, but no chrysophanol.

Isolation of a Phytosterolin, $C_{33}H_{56}O_6$.

The ethereal liquid which had been extracted with aqueous alkalis, as above described, was washed with water, when a considerable amount of dark green material was removed. The washings were acidified, and extracted with ether, and the sparingly soluble solid which had separated was then collected on a filter and washed with ether. This solid was thoroughly examined, but appeared to consist only of chlorophyll and resinous matter. The ethereal filtrate was then extracted with fairly concentrated aqueous potassium hydroxide, when small amounts of rhein and aloe-emodin were obtained. After this treatment it was washed with water, which removed a large quantity of a dark green product, whilst some neutral substance which had been occluded in the material removed by the first washing with water, described above, remained dissolved in the ether, and was added to the main bulk of the neutral constituents of the petroleum extract. The aqueous washings were acidified, and extracted with ether, when some sparingly soluble solid which separated in the form of an emulsion was collected, and well washed with ether. The solid was dried, and extracted in a Soxhlet apparatus for a long time with ethyl acetate, after which the boiling liquid was separated by filtration from some sparingly soluble solid. In this way a large amount of chlorophyll and resinous material was removed. The sparingly soluble solid separated from dilute pyridine as a black, amorphous powder, but gave a colour reaction, indicating that it contained a phytosterolin. It was therefore acetylated by heating with acetic anhydride in the presence of pyridine, when the resulting acetyl derivative crystallised from alcohol in dark-coloured leaflets. This material, after treatment with animal charcoal and repeated crystallisation from alcohol, was finally obtained in colourless, glistening leaflets, melting at 163°.

On hydrolysis with potassium hydroxide this acetyl derivative

yielded a substance which crystallised from dilute pyridine in small tufts of colourless, microscopic needles, melting at about 290°:

0·0909 gave 0·2403 CO_2 and 0·0854 H_2O. C=72·1; H=10·4.
$C_{33}H_{56}O_6$ requires C=72·3; H=10·2 per cent.

This substance was thus identified as a phytosterolin (phytosterol glucoside).

The acetyl derivative, on analysis, gave the following result:

0·1076 gave 0·2727 CO_2 and 0·0879 H_2O. C=68·9; H=9·2.
$C_{33}H_{52}O_6(CO{\cdot}CH_3)_4$ requires C=68·7; H=8·9 per cent.

The original ethereal filtrate from the crude phytosterolin was evaporated, and the very dark green, oily residue dissolved in methyl alcohol, and esterified by means of sulphuric acid. The mixture was then cooled, and filtered, which removed some resin and a quantity of a dark green, amorphous solid of low melting point, which could not be distilled. The methyl-alcoholic filtrate was then poured into water, the mixture extracted with ether, and the ethereal liquid deprived of a considerable amount of chlorophyll and a little unesterified acid by shaking with aqueous alkali, and subsequently washing with water. The ethereal solution was then evaporated, and the residue, which represented the crude methyl esters of the free fatty acids, purified by distillation under diminished pressure. The esters, which amounted to about 15 grams, were thus obtained as a pale brown oil, which was examined in connexion with the corresponding product from the combined acids, as described below.

Examination of the Fatty Acids.

The ethereal solutions of the neutral portion of the petroleum extract of the resin were united, and the solvent removed. The residue was then dissolved in alcohol, and hydrolysed by means of potassium hydroxide. After removing the greater part of the solvent, the mixture was poured into water, and then extracted many times with ether, for the removal of the unsaponifiable constituents. The alkaline aqueous liquid was then acidified, and extracted with ether, when a quantity of a sparingly soluble, dark-coloured solid separated in the lower portion of the ethereal layer. This solid was collected, and, when submitted to a process of purification analogous to that employed for the isolation of the previously-described phytosterolin, it yielded a further quantity of the latter. The ethereal filtrate was concentrated to a small bulk, and then largely diluted with petroleum, when a considerable amount of chlorophyll was precipitated, which was discarded. The ether-

petroleum liquid was then evaporated, and the residue dissolved in methyl alcohol, and esterified by means of sulphuric acid. On cooling the mixture a quantity of a dark green, wax-like solid separated, which was collected. This solid, on examination, was found to consist of chlorophyll, together with myricyl alcohol, which had escaped extraction during the removal of the unsaponifiable material. The methyl-alcoholic filtrate was poured into water, and the mixture extracted with ether, the resulting ethereal solution being deprived of some unesterified acid and much chlorophyll by extracting it with aqueous potassium hydroxide, and subsequently washing it with water. The ethereal liquid was then evaporated, and the residue purified by distillation under diminished pressure, when a quantity (about 15 grams) of a pale brown liquid was obtained. This portion of methyl ester, together with that previously obtained from the free fatty acids, was then fractionally distilled five times under diminished pressure, when the following fractions were obtained: Below 240°; 240—250°; 250—260°; above 260°/60 mm.

The fraction boiling below 240° represented about one-third of the total material, and consisted of methyl palmitate (m. p. 29°). On hydrolysis it yielded palmitic acid, which formed colourless plates melting at 62·5°. (Found, C=74·8; H=12·5. Calc., C=75·0; H=12·5 per cent.)

The fraction boiling at 240—250°/60 mm. was somewhat larger than the preceding one. On hydrolysis it yielded a mixture, which contained a small proportion of unsaturated acid, but consisted for the most part of palmitic acid, together with apparently a little stearic acid.

The portion of the material distilling at 250—260°/60 mm., when hydrolysed, gave a small amount of unsaturated acid, together with a solid acid. The latter, when crystallised five times alternately from alcohol and ethyl acetate, yielded stearic acid melting at 69°. (Found, C=75·9; H=12·7. Calc., C=76·1; H=12·7 per cent.)

The fraction of ester boiling above 260°/60 mm. was too small for examination.

Examination of the Unsaponifiable Material.

The combined ethereal extracts containing the unsaponifiable material, which had been obtained as above described, were washed, dried, and evaporated. The residue was then heated with a large amount of alcohol, and the mixture filtered whilst hot, thereby removing a quantity of almost black, tarry material. The filtrate, which was dark brown, deposited, on cooling, a quantity of an

indistinctly crystalline solid, which was collected, and again crystallised from alcohol. This was then crystallised once from ethyl acetate, and distilled under diminished pressure, when it passed over at a high temperature as an almost colourless liquid, which solidified on cooling. The distillate was then crystallised twice from ethyl acetate, with the employment of animal charcoal, when a quantity (about 8 grams) of small, colourless leaflets, melting at 83°, was obtained. (Found, C=82·1; H=14·5. $C_{30}H_{62}O$ requires C=82·2; H=14·5 per cent.)

This substance was therefore myricyl alcohol.

Isolation of a Phytosterol, $C_{27}H_{46}O$.

The combined alcoholic mother liquors from the crude myricyl alcohol were diluted somewhat with water, and kept for some time, when a quantity of crystalline material, together with much orange-red-coloured oil, was deposited. The solid was collected, when it was found to be a mixture of myricyl alcohol, and a substance which appeared to be a phytosterol. The myricyl alcohol was eliminated by fractional crystallisation from warm ethyl acetate, in which it was more sparingly soluble than the phytosterol. A product was then finally obtained, which, when crystallised from a mixture of ethyl acetate and dilute alcohol, formed large, lustrous plates, melting at 142—143°:

0·2932, on heating at 130°, lost 0·0162 H_2O. H_2O=5·5.

0·0986 * gave 0·2967 CO_2 and 0·1033 H_2O. C=83·6; H=11·9.

$C_{27}H_{46}O,H_2O$ requires H_2O=4·5 per cent.

$C_{27}H_{46}O$ requires C=83·9; H=11·9 per cent.

The optical rotation of the phytosterol was determined, with the following result:

0·2770,* made up to 20 c.c. with chloroform, gave α_D $-1°3'$ in a 2-dcm. tube, whence $[\alpha]_D$ $-37·8°$.

This phytosterol yielded an acetyl derivative, which formed pearly leaflets, melting at 128°.

The filtrate from the crude phytosterol, which contained the greater part of the unsaponifiable material, was carefully examined, but only orange-coloured, oily products could be obtained from it.

Ether, Chloroform, Ethyl Acetate, and Alcohol Extracts of the Resin.

The ether extract of the resin was a dark, brownish-green mass, and amounted to 14·4 grams. On examination it was found to contain, in addition to chlorophyll, some fatty matter, myricyl

* Dried at 130°.

...hol, and a considerable proportion of rhein and aloe-emodin, ...ut no kaempferol was present.

The chloroform extract of the resin amounted to only 3 grams, ...d consisted of a dark greenish-brown resin.

The ethyl acetate extract amounted to 2 grams, and was similar ...n character to the last-mentioned extract.

The alcohol extract was a dark brown resin, amounting to ...0 grams, and nothing definite could be obtained from it.

II. *Senna Leaves from Peru.*

This material consisted of a sample of senna leaves which had ...een obtained from Lima, Peru, and concerning which the following ...nformation was supplied: "During the last few years there has ...een introduced into England, from Port Royal (Jamaica), and ...ecently from the interior of Peru, a new species of senna (*Cassia ...nceolata*, var. *Porturregalis*), the characters of which are as ...llows: The flavour of its infusion, which is clear, and nearly ...olourless, much resembles that of tea. It is very purgative, and at ...he same time it is not nauseous, nor does it cause griping or irrita...on. On account of these properties it is much valued for the ...ebilitated, the aged, women, and children."

A sample of these leaves, together with buds, flowers, and pods, ...as submitted to Mr. E. M. Holmes, F.L.S., who kindly compared ...em with specimens at Kew and at the British Museum, when ...hey were found to be, botanically, quite identical with well-...eveloped specimens of Tinnevelly senna (*Cassia angustifolia*, ...ahl). As is shown below, they differed somewhat from the Tinne...elly senna leaves, the examination of which has just been ...escribed, both in the amount of resin, the proportions of the ...arious extracts, and in some of their constituents. The differences ...bserved, however, are only such as might be accounted for by ...he altered conditions of climate and soil.

As a preliminary experiment, a portion (20 grams) of the ground ...eaves was extracted successively in a Soxhlet apparatus with ...arious solvents, when the following amounts of extract, dried at ...00°, were obtained:

Petroleum (b. p. 35—50°) extracted	0·82 gram	=	4·10 per cent.
Ether	,,	0·70 ,,		3·50 ,,
Chloroform	,,	0·26 ,,		1·30 ,,
Ethyl acetate	,,	0·47 ,,		2·35 ,,
Alcohol	,,	2·25 ,,		11·25 ,,
	Total =	4·50 grams	=	22·50 per cent.

A quantity (3·365 kilograms) of the ground leaves was then ...oroughly extracted in a large Soxhlet apparatus with boiling

alcohol, after which the resulting extract was concentrated, and examined in a manner analogous to that described in connexion with the investigation of the Tinnevelly leaves.

A small amount of essential oil was removed by means of steam, after which the resin was separated from the water-soluble constituents. The aqueous liquid was extracted first with ether, and subsequently with amyl alcohol, after which it was found to contain considerable sugar, together with amorphous products, which yielded kaempferol on hydrolysis.

The ethereal extract, on examination, yielded, in addition to some amorphous products, aloe-emodin, rhein, and a product having the properties of a flavone derivative. The latter was, however, in part, much more sparingly soluble in alcohol than the corresponding material from the Tinnevelly leaves. The portion which was sparingly soluble crystallised from alcohol in small, yellow needles, melting at 302°. (Found, C=60·9; H=4·1. $C_{16}H_{12}O_7$ requires C=61·2; H=3·8 per cent.)

This substance was found to be identical with *iso*rhamnetin, which was first isolated by A. G. Perkin (T., 1896, **69**, 1658) from the flowers of the yellow wallflower, and subsequently by Power and Salway from red clover flowers (T., 1910, **97**, 245). The melting point observed in the present instance is, however, a little higher than that previously recorded. The substance yielded tetra-acetyl*iso*rhamnetin, which formed thin, colourless needles, melting at 201°.

The alcoholic mother liquors from the *iso*rhamnetin gave a product which, when acetylated, yielded tetra-acetylkaempferol identical with that obtained from the Tinnevelly leaves. It crystallised from alcohol with half a molecule of solvent of crystallisation.

0·1421,* on heating at 130°, lost 0·0062 C_2H_6O. C_2H_6O = 4·6.

$C_{23}H_{15}O_{10},\frac{1}{2}C_2H_6O$ requires C_2H_6O = 4·8 per cent.

The amyl alcohol extract of the aqueous liquid yielded some viscid, brown material, which was readily soluble in amyl alcohol, and a yellow, amorphous product, sparingly soluble in dry amyl alcohol. The viscid material, on treatment with alkali, yielded *iso*rhamnetin and kaempferol, the latter preponderating, whilst the sparingly soluble, yellow product was found to be a mixture of glucosides. It would not crystallise, and no individual substance could be separated from it. On hydrolysis with dilute aqueous sulphuric acid it yielded dextrose, rhein, *iso*rhamnetin, kaempferol, and aloe-emodin.

* Air-dried substance.

Examination of the Resin.

The resin was a soft, dark green mass, and amounted to 136 grams, being thus equivalent to 5·8 per cent. of the weight of the leaves employed.

The petroleum extract, which amounted to 137 grams, yielded, in addition to chlorophyll and amorphous products, the following definite substances: Myricyl alcohol (m. p. 83°); a phytosterol, $C_{27}H_{46}O$ (m. p. 142—143°); a phytosterolin, $C_{33}H_{56}O_6$; rhein; aloe-emodin; palmitic and stearic acids, and a small amount of unsaturated acid. Chrysophanol was absent.

The ether extract amounted to 18·5 grams. It consisted chiefly of resinous material and chlorophyll, but also yielded small amounts of rhein, aloe-emodin, and the above-mentioned mixture of flavone derivatives.

The chloroform, ethyl acetate, and alcohol extracts of the resin amounted to 9, 7, and 24 grams respectively. They all consisted of black, amorphous masses, and nothing definite could be isolated from any of them.

III. *Alexandrian Senna Leaves.*

In order to make the present investigation complete, it was deemed desirable also to make an examination of Alexandrian senna leaves, especially on account of the fact that Tschirch and Hiepe (*loc. cit.*) have stated that senna leaves contain "senna-emodin," which was considered to be identical with aloe-emodin, "senna-*iso*emodin," "sennarhamnetin," and "sennachrysophanic acid" (chrysophanol). In the present case no attempt was made to conduct a complete examination of the leaves, attention being chiefly directed to the examination of the anthraquinone and flavone derivatives, and their glucosides.

Ten pounds of a good quality of Alexandrian senna leaves were ground, and extracted in a large Soxhlet apparatus, first with ether, and then with alcohol, the resulting extracts being subsequently examined in the direction indicated, with the employment of methods similar to those already described. It was then found that the anthraquinone derivatives present consisted solely of rhein and aloe-emodin, whilst the flavone derivatives were *iso*rhamnetin and kaempferol, the former preponderating. These four substances were also found to be present in the form of glucosides, and in much greater proportion as such than in the free state. Myricyl alcohol and a phytosterolin were also isolated.

Summary.

The results of the present investigations may be summarised as follows:

The material employed consisted of (I) Tinnevelly senna leaves (*Cassia angustifolia*, Vahl); (II) senna leaves from Lima, Peru, which were found to be botanically identical with the Tinnevelly leaves; (III) Alexandrian senna leaves. The last-mentioned species is usually recognised as *Cassia acutifolia*, Delile, but by some authorities it is regarded simply as a variety of *Cassia angustifolia*.

(I) An alcoholic extract of the Tinnevelly leaves, when distilled with steam, yielded a small amount of an essential oil. From the portion of the extract which was soluble in water the following substances were isolated: (i) Salicylic acid, (ii) rhein, $C_{15}H_8O_6$; (iii) kaempferol, $C_{15}H_{10}O_6$; (iv) aloe-emodin, $C_{15}H_{10}O_5$; (v) *kaempferin*, $C_{27}H_{30}O_{16},6H_2O$ (m. p. 185—195°), a new glucoside of kaempferol; (vi) a mixture of the glucosides of rhein and aloe-emodin; (vii) the magnesium salt of an unidentified organic acid. The aqueous liquid furthermore contained a quantity of a sugar which yielded *d*-phenylglucosazone (m. p. 216°), and some brown, amorphous products, which, on treatment with alkali, gave kaempferol, together with small amounts of rhein and aloe-emodin. Some amorphous, glucosidic material was also present.

The portion of the alcoholic extract which was insoluble in water consisted of a soft, dark green resin, which amounted to 7·0 per cent. of the weight of the leaves employed. From this material, which contained considerable chlorophyll and amorphous products, there were isolated, in addition to some of the substances mentioned above, the following compounds: (i) Myricyl alcohol; (ii) a phytosterol, $C_{27}H_{46}O$; (iii) a phytosterolin, $C_{33}H_{56}O_6$; (iv) palmitic and stearic acids.

(II) The senna leaves from Lima, Peru, were found to contain all the above-mentioned compounds, with the exception of the magnesium salt, and, in addition, *iso*rhamnetin. A glucoside of *iso*rhamnetin was also present in association with glucosides of kaempferol, rhein, and aloe-emodin, but no pure compound could be isolated from the mixture.

(III) Alexandrian senna leaves yielded, in addition to myricyl alcohol and a phytosterolin, rhein, aloe-emodin, kaempferol, and *iso*rhamnetin. These four substances were also present in the form of glucosides, and in much greater proportion as such than in the free state.

The statements of Tschirch and Hiepe (*Arch. Pharm.*, 1900, **238**, 427) that senna leaves contain "senna*iso*emodin," "senna

irysophanic acid" (chrysophanol), and a "substance, $C_{14}H_{10}O_5$," ould not be confirmed, it having been ascertained that the anthra-uinone derivatives present consist solely of rhein and aloe-emodin. this connexion it may be noted that a mixture of approximately qual quantities of the last-mentioned two compounds has the mpirical composition and properties assigned by Tschirch and iepe to the "substance, $C_{14}H_{10}O_5$." Furthermore, the "senna-hamnetin" of the last-mentioned authors has been found to be lentical with the *iso*rhamnetin previously described by Perkin T., 1896, **69**, 1658).

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

CONTENTS.

PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS:—

PART I.

Organic Chemistry.

Physiological Chemistry.

Chemistry of Vegetable Physiology and Agriculture.

PART II.

General and Physical Chemistry.

Inorganic Chemistry.

Mineralogical Chemistry.

Analytical Chemistry.

INDEX OF AUTHORS' NAMES

IN TRANSACTIONS AND ABSTRACTS

C.

D.

E.

I.

J.

K.

L.

U.

V.

W.

Y.

Z.

ERRATA.

Collective Index 1903—1912 (Authors).

Page.	Line.	
[illegible]	25	col. ii, *for* "1909" *read* "1908."

Vol. CIII (Trans., 1913).

[illegible]	19	*for* "bromobenzene" *read* "bromonaphthalene."
[illegible]	1	,, "marked" ,, "masked."

Vol. CIV (Abstr., 1913).

[illegible]	21	*for*	"Alfons"	*read*	"Adolf."
[illegible]	7	,,	"Mendell"	,,	"Mendel."
[illegible]	8	,,	"Wakemann"	,,	"Wakeman."
[illegible]	22	,,	"L."	,,	"E."
[illegible]	19*	,,	"A."	,,	"E."
[illegible]	9				
	17*	,,	"Houston"	,,	"Houstoun."
[illegible]	14				
[illegible]	16	,,	"Kammerlingh"	,,	"Kamerlingh."
[illegible]	22	,,	"Gehloff"	,,	"Gehlhoff."
[illegible]	23	,,	"19"	,,	"14."
[illegible]	17	,,	"Torn"	,,	"Horn."

* From bottom.

Examination of the Resin.

The resin was a soft, dark green mass, and amounted to 196 grams, being thus equivalent to 5·8 per cent. of the weight of the leaves employed.

The petroleum extract, which amounted to 137 grams, yielded, in addition to chlorophyll and amorphous products, the following definite substances: Myricyl alcohol (m. p. 83°); a phytosterol, $C_{27}H_{46}O$ (m. p. 142—143°); a phytosterolin, $C_{33}H_{56}O_6$; rhein; aloe-emodin; palmitic and stearic acids, and a small amount of unsaturated acid. Chrysophanol was absent.

The ether extract amounted to 18·5 grams. It consisted chiefly of resinous material and chlorophyll, but also yielded small amounts of rhein, aloe-emodin, and the above-mentioned mixture of flavone derivatives.

The chloroform, ethyl acetate, and alcohol extracts of the resin amounted to 9, 7, and 24 grams respectively. They all consisted of black, amorphous masses, and nothing definite could be isolated from any of them.

III. *Alexandrian Senna Leaves.*

In order to make the present investigation complete, it was deemed desirable also to make an examination of Alexandrian senna leaves, especially on account of the fact that Tschirch and Hiepe (*loc. cit.*) have stated that senna leaves contain "senna-emodin," which was considered to be identical with aloe-emodin, "senna-*iso*emodin," "sennarhamnetin," and "sennachrysophanic acid" (chrysophanol). In the present case no attempt was made to conduct a complete examination of the leaves, attention being chiefly directed to the examination of the anthraquinone and flavone derivatives, and their glucosides.

Ten pounds of a good quality of Alexandrian senna leaves were ground, and extracted in a large Soxhlet apparatus, first with ether, and then with alcohol, the resulting extracts being subsequently examined in the direction indicated, with the employment of methods similar to those already described. It was then found that the anthraquinone derivatives present consisted solely of rhein and aloe-emodin, whilst the flavone derivatives were *iso*rhamnetin and kaempferol, the former preponderating. These four substances were also found to be present in the form of glucosides, and in much greater proportion as such than in the free state. Myricyl alcohol and a phytosterolin were also isolated.

Summary.

The results of the present investigations may be summarised as follows:

The material employed consisted of (I) Tinnevelly senna leaves (*Cassia angustifolia*, Vahl); (II) senna leaves from Lima, Peru, which were found to be botanically identical with the Tinnevelly leaves; (III) Alexandrian senna leaves. The last-mentioned species is usually recognised as *Cassia acutifolia*, Delile, but by some authorities it is regarded simply as a variety of *Cassia angustifolia*.

(I) An alcoholic extract of the Tinnevelly leaves, when distilled with steam, yielded a small amount of an essential oil. From the portion of the extract which was soluble in water the following substances were isolated: (i) Salicylic acid, (ii) rhein, $C_{15}H_8O_6$; (iii) kaempferol, $C_{15}H_{10}O_6$; (iv) aloe-emodin, $C_{15}H_{10}O_5$; (v) *kaempferin*, $C_{27}H_{30}O_{16},6H_2O$ (m. p. 185—195°), a new glucoside of kaempferol; (vi) a mixture of the glucosides of rhein and aloe-emodin; (vii) the magnesium salt of an unidentified organic acid. The aqueous liquid furthermore contained a quantity of a sugar which yielded *d*-phenylglucosazone (m. p. 216°), and some brown, amorphous products, which, on treatment with alkali, gave kaempferol, together with small amounts of rhein and aloe-emodin. Some amorphous, glucosidic material was also present.

The portion of the alcoholic extract which was insoluble in water consisted of a soft, dark green resin, which amounted to 7·0 per cent. of the weight of the leaves employed. From this material, which contained considerable chlorophyll and amorphous products, there were isolated, in addition to some of the substances mentioned above, the following compounds: (i) Myricyl alcohol; (ii) a phytosterol, $C_{27}H_{46}O$; (iii) a phytosterolin, $C_{33}H_{56}O_6$; (iv) palmitic and stearic acids.

(II) The senna leaves from Lima, Peru, were found to contain all the above-mentioned compounds, with the exception of the magnesium salt, and, in addition, *iso*rhamnetin. A glucoside of *iso*rhamnetin was also present in association with glucosides of kaempferol, rhein, and aloe-emodin, but no pure compound could be isolated from the mixture.

(III) Alexandrian senna leaves yielded, in addition to myricyl alcohol and a phytosterolin, rhein, aloe-emodin, kaempferol, and *iso*rhamnetin. These four substances were also present in the form of glucosides, and in much greater proportion as such than in the free state.

The statements of Tschirch and Hiepe (*Arch. Pharm.*, 1900, **238**, 427) that senna leaves contain "senna*iso*emodin," "senna-

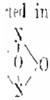
chrysophanic acid" (chrysophanol), and a "substance, $C_{14}H_{10}O_5$," could not be confirmed, it having been ascertained that the anthraquinone derivatives present consist solely of rhein and aloe-emodin. In this connexion it may be noted that a mixture of approximately equal quantities of the last-mentioned two compounds has the empirical composition and properties assigned by Tschirch and Hiepe to the "substance, $C_{14}H_{10}O_5$." Furthermore, the "sennarhamnetin" of the last-mentioned authors has been found to be identical with the *iso*rhamnetin previously described by Perkin (T., 1896, **69**, 1658).

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

CXIV.—*The Conversion of Orthonitroamines into* iso*Oxadiazole Oxides (Furoxans).*

By ARTHUR GEORGE GREEN and FREDERICK MAURICE ROWE.

the two previous communications (T., 1912, **101**, 2452; this .. p. 897) it has been shown that many *o*-nitroamines on oxida- n by means of sodium hypochlorite in alkaline solution are con- ted into furoxans (furazan oxides), to which the constitution

 is now attributed.

In order to investigate the limits of this reaction and the extent which it is influenced by substitution of hydrogen in the para- sition, we have now studied the action of alkaline sodium hypo- lorite on the following compounds: 2:4-Dinitroaniline, nitro-*p*- enylenediamine, 2-nitro-4-acetyl-*p*-phenylenediamine, 3-nitro-4- inobenzeneazo-β-naphthol, *o*-nitroaniline-*p*-sulphonic acid, and initrobenzidine. These compounds may be regarded as deriv- ves of *o*-nitroaniline, in which the para-hydrogen atom is replaced the nitro-, amino-, acetylamino-, azonaphthol, sulphonic, and enyl groups respectively. It has already been shown in the case dinitroaniline that when the oxidation is effected in methyl- or -alcoholic solution the formation of the furoxan is accom- nied by a remarkable replacement of the *p*-nitro-group by thoxyl or ethoxyl, a fact which confirms the hypothesis that the ction is a quinonoid one, recalling the ready replacement of

electronegative groups in the quinonoid nucleus, as, for example, of the sulphonic group in β-naphthaquinonesulphonic acid. A variety of experiments, which have since been performed, have demonstrated that the p-nitro-group in dinitroaniline cannot in any circumstances be preserved intact. When the oxidation is effected in absence of an alcohol by employing a fine aqueous suspension of the base in place of an alcoholic solution, no product at all could be isolated, and judging from the large amount of chloropicrin produced, the benzene nucleus was completely destroyed. A similar result was obtained on submitting to oxidation with sodium hypochlorite aqueous solutions of nitro-p-phenylenediamine, nitroacetyl-p-phenylenediamine, and the azo-compound obtained by combining diazotised nitro-p-phenylenediamine with β-naphthol. In all these instances oxidation took place readily, but apparently with complete disruption of the ring, since a strong odour of chloropicrin was always observed, and nothing could be isolated from the solution. This was the case whether the oxidation was effected at 15° or at 0°, and whether in an alcoholic or in aqueous solution. Very much the same result was obtained by the oxidation of o-nitroaniline-p-sulphonic acid, although in this instance it was found possible to isolate a small quantity of a compound which appeared to be the furoxansulphonic acid, $SO_3H{\cdot}C_6H_3{:}N_2O_2$. The greater part of the product, however, suffered complete destruction, and much sodium sulphate was obtained. It might have been anticipated that o-nitroaniline-sulphonic acid would have behaved on oxidation in an alcoholic solution similarly to dinitroaniline, an alkyloxy-group taking the place of the sulphonic group, but no trace of such a product could be detected.

It appears, therefore, that the amino-, acetylamino-, azo-, and sulphonic groups (and in aqueous solution also the nitro-group), when occupying the para-position with respect to the amino-group in a substituted o-nitroaniline, render the benzene ring unstable to hypochlorite oxidation. On the other hand, we have previously shown that the stability of the ring is not diminished by the presence of a chlorine atom or methyl group.

The oxidation of o-dinitrobenzidine appeared to offer considerable interest both from the above point of view and also on account of the apparent existence of this base in two isomeric forms, as recently pointed out by Cain, Coulthard, and Micklethwait (T., 1912, **101**, 2298). We have therefore submitted the two isomerides under like conditions of reaction to the hypochlorite oxidation, and have obtained the following remarkable result. The dinitrobenz

dine melting at 275°, which Cain regards as a 3:5′-form, produces typical furoxan (bisbenz*iso*oxadiazole oxide),

$$O_2\lessgtr\substack{N\\N}>C_6H_3\cdot C_6H_3<\substack{N\\N}\gtrless O_2,$$

hich is a pale yellow substance, readily convertible into a iphenoquinonetetraoxime, $C_6H_3(:NOH)_2\cdot C_6H_3(:NOH)_2$, and a bisenz*iso*oxadiazole, $O<\substack{N\\|\\N}>C_6H_3\cdot C_6N_3<\substack{N\\|\\N}>O$ On the other hand, he isomeride melting at 233°, regarded by Cain as the 3:3′-form, ives no furoxan, but a reddish-orange, crystalline compound of he formula $C_{12}H_6O_4N_4$, which is probably an internal azo-derivtive, $\begin{matrix}C_6H_3(NO_2)\cdot N\\ | \qquad\quad \| \\ C_6H_3(NO_2)\cdot N\end{matrix}$.

Neither of the hypotheses hitherto advanced to account for this nteresting form of isomerism would seem adequate to give an xplanation of this result. Especially untenable is the view of ain, Macbeth, and Stewart (this vol., p. 586), based on the bsorption spectra of the two isomerides, for even if the two contitutions suggested were not interconvertible, which is difficult believe possible, the hemi-quinonoid arrangement should give at ast a monofuroxan. It seems possible that an explanation might e based on the formula for benzidine with superimposed nuclei ggested by Kaufler (*Ber.*, 1907, **40**, 3250), but the matter requires rther investigation.

Finally we have submitted to re-examination the so-called "nitrodinitrosobenzene," $NO_2\cdot C_6H_3:N_2O_2$, and "dinitro-*o*-dinitrosoenzene," $C_6H_2(NO_2)_2:N_2O_2$, obtained by Drost (*Annalen*, 1899, 07. 51) by nitration of benz*iso*oxadiazole (then termed *o*-dinitrosoenzene). The fact that the latter of these compounds is stated to ive rise to salts of the type $C_6H(NO_2)_2N_2O_2M'$ seemed to call in uestion the correctness of the constitution assigned, and to render e investigation desirable. The two compounds were readily btained by nitration of the benz*iso*oxadiazole (benzfuroxan) repared by hypochlorite oxidation of *o*-nitroaniline. As thus repared, they exhibited all the properties ascribed to them by rost, and gave on analysis numbers corresponding with the monond di-nitro-derivatives of benz*iso*oxadiazole,

$$C_6H_3(NO_2)<\substack{N\\N}\gtrless O_2 \text{ and } C_6H_2(NO_2)_2<\substack{N\\N}\gtrless O_2.$$

Both compounds were found to possess somewhat strongly-developed cid properties, rendering Congo paper blue and decomposing arbonates. By treatment with potassium hydrogen carbonate, the initro-compound was converted into the yellow, crystalline

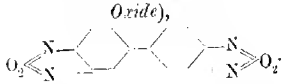
potassium salt described by Drost. This gave on analysis numbers corresponding with the empirical formula $C_6HK(NO_2)_2:N_2O_2$, and on treatment with dilute sulphuric acid was reconverted into the parent compound, of which it is therefore a true salt. A corresponding salt could not be isolated from the mononitro-derivative, although this dissolves readily in alkalis, and also gives a reddish-brown precipitate on adding sodium ethoxide to its benzene solution. Both the mono- and the di-nitro-compounds readily suffer destructive decomposition by dilute alkalis, especially alkali hydroxide, in which they dissolve freely, giving deep red solutions and producing nitrites and ammonia. For this reason all attempts to convert them into the corresponding nitro-o-dioximes proved unsuccessful. The failure to obtain the latter compounds affords, however, no sufficient ground for doubting the correctness of the formulæ assigned, and we seem to have here a case in which strong acidic properties are evidenced by hydrogen in the benzene ring.

Experimental.

o-*Dinitrobenzidines.*

The two isomeric o-dinitrobenzidines were prepared as described by Brunner and Witt (*Ber.*, 1887, **20**, 1023) and by Bandrowski (*Ber.*, 1884, **17**, 1181) respectively. It was found that the two compounds could be readily separated from each other, and quickly obtained in a pure state by making use of the large difference in basicity which exists between them. Whilst the isomeride melting at 275°, which is obtained by the nitration of diacetylbenzidine, is entirely precipitated as free base when its solution in nearly concentrated hydrochloric acid is diluted with water (thus closely resembling o-nitroaniline), a similar solution of the isomeride melting at 233°, obtained by the nitration of diphthalylbenzidine, is not basified on dilution, and requires to be precipitated by alkali. The two bases possessed the appearance and melting points assigned to them by Cain, Coulthard, and Micklethwait.

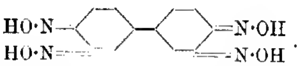
Bisbenzisooxadiazole Oxide (Bisbenzfuroxan or Bisbenzfurazan Oxide),



o-Dinitrobenzidine (m. p. 275°), converted into a finely-divided precipitate by solution in concentrated sulphuric acid, dilution with water, and washing free from acid, was made into a paste with sodium hydroxide solution (40 per cent. NaOH), and treated with

excess of sodium hypochlorite (10 per cent. active chlorine). The xture was then slowly heated to the boiling point. At a tempera-e of about 95° the suspended dinitrobenzidine changed in colour m a deep red to a pale buff-yellow. The mixture was boiled until further lightening of tint took place, and the precipitate was then lected and washed with water. If it still contains any unaltered itrobenzidine, this can be removed by extraction with boiling centrated hydrochloric acid. The product is a pale yellow pre-itate, insoluble in water, very sparingly soluble in alcohol, more dily so in acetone, and easily soluble in hot pyridine, tetrachloro-ane, or chlorobenzene. The latter is the best medium for crystal-ation, and from it the compound was obtained in thin, yellow, cagonal plates, melting at 211°. It is not volatile with steam, and solves in concentrated sulphuric acid to a yellow solution, from ich it is reprecipitated by water:

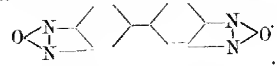
)·0654 gave 11·95 c.c. N_2 at 25° and 751 mm. N = 20·84.
$C_{12}H_6O_4N_4$ requires N = 20·74 per cent.

Diphenoquinonetetraoxime, 

Four grams of the pure bisbenz*iso*oxadiazole oxide were dissolved concentrated sulphuric acid and poured into water. The finely-vided product was collected, washed free from acid, and -pended in water. Six grams of hydroxylamine hydrochloride re then added, and after warming to about 50°, aqueous sodium droxide was run in until complete solution occurred. Care must taken that the temperature does not rise too high, as the oxime is rapidly converted into the bisbenz*iso*oxadiazole at tem-ratures above 60°. The blood-red solution after filtration was idified with acetic acid, when the dioxime separated as a colloidal ecipitate, which it was not found possible to crystallise. When y it forms a brown, amorphous powder, melting at 235°, very aringly soluble in organic solvents, but dissolving readily in kalis or concentrated acids, giving red solutions. It has weak ordant dyeing properties. On oxidation with sodium hypochlorite is reconverted into bisbenz*iso*oxadiazole oxide, and on heating th alkalis into bisbenz*iso*oxadiazole:

0·0582 gave 10·45 c.c. N_2 at 22° and 748 mm. N = 20·61.
$C_{12}H_{10}O_4N_4$ requires N = 20·44 per cent.

Bisbenzisooxadiazole (Bisbenzfurazan),



The caustic alkaline solution of the bisdioxime was heated until it was nearly colourless. The precipitated bisbenz*iso*oxadiazole was collected, washed, dried, and recrystallised from glacial acetic acid, and then from chlorobenzene. It forms yellow needles, which melt at 244°. It dissolves in concentrated sulphuric acid with a yellow colour, and is precipitated unchanged as a nearly colourless precipitate on addition of water:

0·0728 gave 15·1 c.c. N_2 at 25° and 751 mm. N=23·67.

$C_{12}H_6O_2N_4$ requires N=23·53 per cent.

Oxidation of Dinitrobenzidine of m. p. 233°.

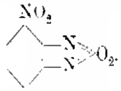
The oxidation with hypochlorite was effected in exactly the same manner as in the case of the other isomeride, but took place with considerably greater difficulty. Instead of becoming paler, the precipitate assumes a darker tint. The product was collected, washed with water, extracted with hydrochloric acid to remove unaltered dinitrobenzidine, and the residue was crystallised from chlorobenzene. The product was thus obtained in bunches of small reddish-orange needles, which darken at 200° and melt at 220°:

0·0804 gave 14·4 c.c. N_2 at 25° and 766 mm. N=20·84.

$C_{12}H_6O_4N_4$ requires N=20·74 per cent.

The substance did not behave like a furoxan, and could not be converted by reduction with alkaline hydroxylamine into a dioxime. It dissolves with a red colour in concentrated sulphuric acid.

*6-Nitrobenz*iso*oxadiazole Oxide (6-Nitrobenzfuroxan),*



Benz*iso*oxadiazole oxide, dissolved in concentrated sulphuric acid, was nitrated in the cold with one molecular proportion of nitric acid (D 1·52), mixed with an equal volume of concentrated sulphuric acid. The product, when crystallised from acetic acid, formed thin, yellowish-brown plates, melting at 143°. It had marked acidic properties:

0·0681 gave 13·7 c.c. N_2 at 19° and 750 mm. N=23·40.

$C_6H_3O_4N_3$ requires N=23·20 per cent.

The alcoholic solution on addition of sodium sulphide gives a deep blue coloration, soon passing into violet and brown.

4:6-*Dinitrobenz*iso*oxadiazole Oxide* (4:6-*Dinitrobenzfuroxan*),

Ten grams of benz*iso*oxadiazole oxide, dissolved in 120—150 c.c. of concentrated sulphuric acid, were nitrated by addition of a mixture of 15 c.c. of nitric acid (D 1·52) and 40 c.c. of concentrated sulphuric acid. The mixture is cooled at first, and then warmed to 40° and poured into water. The product, when crystallised from acetic acid, forms large, yellow needles, melting at ...°. It has pronounced acid properties, turning Congo paper blue, and dissolving easily in aqueous alkali. The alkaline solutions readily undergo decomposition, with formation of ammonia and nitrites:

0·1292 gave 27·7 c.c. N_2 at 19° and 750 mm. N = 24·93.

$C_6H_2O_6N_4$ requires N = 24·78 per cent.

The potassium salt, prepared as described by Drost, was obtained in yellowish-brown, glistening plates soluble in water.

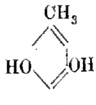
Department of Tinctorial Chemistry,
The University, Leeds.

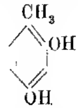
CCXV.—*Substituted Dihydroresorcins. 1-Methyldihydroresorcin and 2-Methyldihydroresorcin.*

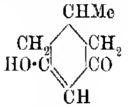
By Charles Gilling.

In the preparation of hydroaromatic compounds from aromatic hydroxy-acids it has been observed that only those compounds which contain the hydroxyl and carboxyl groups in the meta-position to one another are susceptible of reduction in the desired way (compare Baudisch, Hibbert, and Perkin, T., 1909, **95**, 1870). It seemed, therefore, to be of interest to ascertain whether a similar rule holds good for the reduction of the dihydroxytoluenes. Unfortunately, most of these compounds are difficult to prepare in quantity, and as the author has found it impracticable to continue the research for the present, it seems desirable to give a brief account of the experiments on the reduction products of orcinol (I) and of cresorcinol (II) so far as they were completed when working in the research laboratory of the Pharmaceutical Society in 1911.

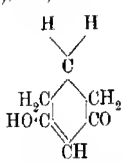
Orcinol was first reduced by Vorländer (*Ber.*, 1897, **30**, 1801), using sodium amalgam, the reduction product being 1-methyldihydroresorcin (III). This compound was also prepared by the same author by condensing ethyl crotonate with ethyl acetoacetate and hydrolysing the resulting ester (*Annalen*, 1899, **308**, 195):

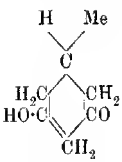

(I.)

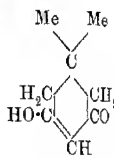

(II.)


(III.)

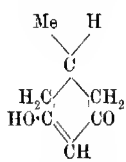
Several new derivatives of this substance are now described, the most interesting of which are those produced by its esterification. Methyldihydroresorcin is the intermediate member of the series, which comprises dihydroresorcin (IV) and dimethyldihydroresorcin (V), but, unlike either, its molecule is unsymmetrical:


(IV.)

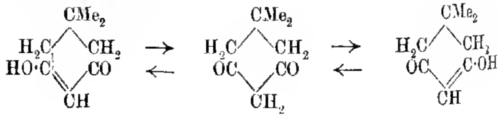

(III.)


(V.)

It would therefore appear that a second form of this substance having the configuration VI should be capable of existence:

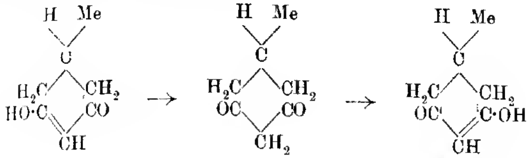

(VI.)

Much evidence has been brought forward to show that dihydro- and dimethyldihydro-resorcins are tautomeric substances; thus they yield monobasic silver salts and dioximes, and from spectroscopic observations it is probable that their molecules, in solution at least, are continually changing from one form to another, as represented in the following scheme:



The introduction of an ethyl group in place of the mobile hydrogen atom destroys this tautomerism.

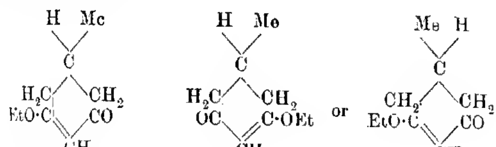
Assuming that 1-methyldihydroresorcin behaves in a similar way, the change will be represented:



(VII.)

and it will be seen that the configuration (VII) is identical with that denoted by (VI), and it follows that 1-methyldihydroresorcin will exist in only one form, a form, however, in which a tautomeric change is continually taking place. This view is in agreement with the observed facts, for although a careful search has been made among the reaction products for a second modification, none was ever found.

When 1-methyldihydroresorcin is esterified with ethyl alcohol and sulphuric acid, the product is a liquid from which crystals can be separated by freezing. Both crystals and mother liquor give similar figures on analysis, except that the former contain a molecule of water of crystallisation, and it seems, therefore, most probable that two ethyl ethers are formed, the ethyl group sometimes entering the molecule in the phase represented by (III) and sometimes in the phase (VII), giving rise to the two compounds (VIII) and (IX), which stand in the relationship of *cis*- and *trans*-forms to one another:



(VIII.) (IX.)

The author intends to investigate more fully than has been done up to the present the preparation of 2-methyldihydroresorcin, since this substance, if the above considerations hold good, should yield four isomeric ethyl ethers.

EXPERIMENTAL.

Preparation of 1-*Methyldihydroresorcin.*

This substance was prepared according to the directions of Vorländer, but it was found that after repeatedly crystallising the crude substance from ethyl acetate it melted at 127° (Vorländer gives 122°) with the formation of a red film on the side of the capillary.

The *silver* salt, prepared in the usual manner, is a lemon-yellow substance, which slowly darkens on exposure to light:

0·2012 gave 0·0927 Ag. Ag = 46·07.

$C_7H_9O_2Ag$ requires Ag = 46·30 per cent.

The *disemicarbazone*, prepared by adding the alcoholic solution to a solution of semicarbazide acetate, is a white, amorphous substance, insoluble in all the ordinary solvents. It darkens when heated to 215°, and decomposes at 225°. For analysis it was well washed with alcohol and dried:

0·1037 gave 31·2 c.c. N_2 at 17° and 754 mm. N = 34·62.

$C_9H_{16}O_2N_6$ requires N = 35·0 per cent.

Esterification of 1-*Methyldihydroresorcin.*

Twenty grams were boiled with 100 c.c. of absolute alcohol and 7·5 grams of sulphuric acid under reflux on the water-bath for six hours. The liquid was poured into water, extracted four times with ether, the ethereal solution washed with dilute sodium hydroxide, then with water, and dried, evaporated, and the residue immediately distilled, when 12·5 grams passed over at 147—152°/36 mm. After two more distillations, the product, which was evidently a mixture of two stereoisomeric modifications of the ethyl ether of 1-methyldihydroresorcin, was analysed:

0·1185 gave 0·3030 CO_2 and 0·0940 H_2O. C = 69·73; H = 8·81.

$C_9H_{14}O_2$ requires C = 70·13; H = 9·09 per cent.

On cooling in a freezing mixture and freely exposing to air, a partial solidification took place, and the whole was spread on a porous plate (*A*), when 6 grams of a solid were obtained. This was crystallised from well-cooled diluted acetone:

0·1023 gave 0·2360 CO_2 and 0·0859 H_2O. C = 62·91; H = 9·33.

$C_9H_{14}O_2,H_2O$ requires C = 62·79; H = 9·30.

3-*Ethoxy*-1-*methyl*-Δ^3-cyclo*hexen*-5-*one* (*form* a) is freely soluble in all the ordinary solvents, but may be crystallised from cold dilute acetone, from which it separates in fine, feathery needles melting at 42°. It has a peculiar, fragrant, and camphoraceous

hour. When placed in a vacuum desiccator it first loses water of crystallisation and liquefies, and afterwards slowly volatilises:

0·6907 lost in six hours 0·0759. $H_2O = 10·09$.

$C_9H_{14}O_2,H_2O$ requires $H_2O = 10·5$ per cent.

The residue then suffered a further loss of 0·01 gram per twenty-four hours. The anhydrous substance is a colourless, oily liquid.

The porous plate (*A*), after removal of the above, was extracted with ether, when, after removing the solvent, 5 grams of an oil were obtained. No further quantity of the above-described crystalline ester could be obtained from this by cooling, adding water, or exposing to a moist atmosphere in a closed vessel for several days, and it is doubtless the second modification of the ethyl ether, although possibly not entirely free from the first form. On remaining for a long time exposed to the air, it deposited crystals which melted at 125° with a red film, nor was this melting point altered by admixture with pure 1-methyldihydroresorcin. This hydrolysis can be more rapidly effected by heating either modification for half-an-hour on the water-bath with an alcoholic solution of sodium hydroxide.

The two ethers were also prepared by heating the silver salt of 1-methyldihydroresorcin suspended in dry benzene with the theoretical amount of ethyl iodide. After removing the silver iodide and evaporating, an oily liquid remained, which partly solidified when cooled in a freezing mixture. The solid, after crystallising from dilute acetone, melted at 42°, and its identity was confirmed by the mixed melting-point method.

Reduction of Cresorcinol.

Cresorcinol (2:4-dihydroxytoluene) was prepared from *o*-toluidine according to the directions of Noelting (*Ber.*, 1884, **17**, 265) and Michael and Grandmougin (*Ber.*, 1893, **26**, 2349). Seventeen grams were boiled with 17 grams of sodium hydrogen carbonate, 100 c.c. of water, and 1000 grams of 2 per cent. sodium amalgam for fifteen hours under reflux in a stream of carbon dioxide. The aqueous liquid was then poured off, a further 20 grams of sodium hydrogen carbonate added, and the whole extracted twice with ether to remove unchanged material. Excess of dilute sulphuric acid was then run in, and the liquid extracted five times with chloroform, the chloroform solution dried over sodium sulphate and evaporated, when a sticky syrup remained. After several weeks a small amount of solid (m. p. 66—70°) separated, but as it was only obtained in very small amount, and as it proved very difficult to crystallise, the crude material was used for the preparation of the following derivative.

2-Methyldihydroresorcinanilide was prepared by dissolving 2 grams of the oil with 1·5 grams of aniline in 20 c.c. of dry benzene, and boiling under reflux for ten hours. On adding a few drops of light petroleum a solid separated, which was crystallised from ethyl acetate:

0·3302 gave 19·4 c.c. N_2 at 14° and 762 mm. N = 6·93.
$C_{13}H_{15}ON$ requires N = 6·96 per cent.

This substance is insoluble in light petroleum, readily soluble in chloroform, and can be crystallised from benzene or ethyl acetate, from which it separates in rosettes of yellowish-sandy needles melting at 162°.

The *disemicarbazone* was prepared by dissolving 1 gram of the crude 2-methyldihydroresorcin in alcohol, and adding a solution of semicarbazide acetate, when a pinkish-white, amorphous substance slowly separated. This was washed with alcohol, and dried:

0·1090 gave 33 c.c. N_2 at 20° and 755 mm. N = 34·63.
$C_9H_{16}O_2N_6$ requires N = 35·0 per cent.

The disemicarbazone is insoluble in all the ordinary solvents, and, when heated, darkens at 220°, and melts and decomposes at 224—225°.

The author wishes to express his thanks to the Research Fund Committee of the Chemical Society for a grant which has in part defrayed the expenses of this investigation.

CCXVI.—*A Study of Some Organic Derivatives of Tin as Regards their Relation to the Corresponding Silicon Compounds. Part II. Condensation Products of Dihydroxydibenzylstannane.*

By Thomas Alfred Smith and Frederic Stanley Kipping.

It has been shown recently (Kipping, T., 1912, **101**, 2108; Robison and Kipping, *loc. cit.*, p. 2142) that the dihydroxy compounds of the molecular formula $SiR_2(OH)_2$ are, as a rule, stable at the ordinary temperature, but that in the presence of relatively small proportions of alkalis or acids they readily undergo condensation, giving open-chain and closed-chain products; diphenylsilicanediol,

ır example, gives the following series of compounds (as well as .hers not yet described):

$HO{\cdot}SiPh_2{\cdot}O{\cdot}SiPh_2{\cdot}OH$
ıhydrobisdiphenylsilicanediol.

$HO{\cdot}SiPh_2{\cdot}O{\cdot}SiPh_2{\cdot}O{\cdot}SiPh_2{\cdot}OH$
Dianhydrotrisdiphenylsilicanediol.

$O\begin{matrix}\diagup SiPh_2{\cdot}O \diagdown \\ \diagdown SiPh_2{\cdot}O \diagup\end{matrix}SiPh_2$
Trianhydrotrisdiphenylsilicanediol.

$O\begin{matrix}\diagup SiPh_2{\cdot}O{\cdot}SiPh_2 \diagdown \\ \diagdown SiPh_2{\cdot}O{\cdot}SiPh_2 \diagup\end{matrix}O$
Tetra-anhydrotetrakisdiphenylsilicanediol.

Now derivatives of tin, having the general formula $SnR_2(OH)_2$, ıve not hitherto been obtained. Although the existence of such mpounds might well be premised from the known relationship ıtween tin and silicon, the only substances which have so far en produced by the hydrolysis of dihalogen derivatives of the pe. SnR_2X_2, are certain oxides of the composition SnR_2O. ırther, the nature of these oxides is quite unknown.

Judging from the fact that all the silicon compounds of the mposition $(SiR_2O)_n$ which have been fully investigated (*loc. cit.*) ıve been shown to be fairly complex closed-chain compounds, it ould seem highly probable that the corresponding tin derivatives ıve analogous structures. Since, moreover, even such moderately mplex silicon compounds as trianhydrotris- and tetra-anhydrotetra-sdiphenylsilicanediol are soluble in many of the ordinary organic lvents, whereas the tin compounds $(SnR_2O)_n$ are insoluble, it ight be inferred that the value of n in the latter case is greater ıan three or four.

The main objects of the work described in this paper were the ·eparation of some dihydroxystannic compounds of the composi-on $SnR_2(OH)_2$, and the study of their relation to the correspond-g oxides; it was believed that the results of such an investigation ould throw some light, not only on the nature of these oxides, $(SnR_2O)_n$, but also on the interesting problems presented by the annic and metastannic acids.

The first point which we investigated was the possibility of reparing dihydroxydibenzylstannane, $Sn(CH_2Ph)_2(OH)_2$, by the ydrolysis of the corresponding dichloride (Smith and Kipping, T., 912, 101, 2553). Although we failed to isolate the dihydroxy-erivative, we obtained some evidence of its existence, and in other spects the results were of considerable interest.

Dichlorodibenzylstannane is hydrolysed by a cold aqueous solu-on of potassium hydroxide, giving a soluble product, apparently potassium derivative, $Sn(CH_2Ph)_2(OK)_2$ or

$$Sn(CH_2Ph)_2(OK)(OH),$$

hich is decomposed by carbonic or acetic acid, with separation f a colourless solid. This substance seems to be the dihydroxy-mpound, $Sn(CH_2Ph)_2(OH)_2$, because, immediately after its pre-

cipitation, like dibenzylsilicanediol (Robison and Kipping, *loc. cit.*), it is rapidly and completely soluble in an aqueous solution of potassium hydroxide. The precipitate, however, very quickly changes; even by the time that it has been separated and washed it has altered to such an extent that, when left in contact with a potassium hydroxide solution, about twenty-four hours elapse before it dissolves completely.

This behaviour of the supposed dihydroxystannic compound is analogous to that of diphenyl- and dibenzyl-silicanediols, both of which undergo condensation to some extent when they are precipitated from solutions of their potassium derivatives under conditions such as those just described; and although the change is much more pronounced in the case of the tin compound than in those of the silicon derivatives, it seems reasonable to infer that the three precipitated substances are all of the same type, and undergo fundamentally similar transformations. If so, it must be concluded that the freshly precipitated tin compound, which, from its method of formation and behaviour, is doubtless the dihydroxy-derivative, rapidly changes into some condensation product analogous to one of the open- or closed-chain silicon compounds mentioned above.

On examination it was found at once that the precipitate differed fundamentally from all the known compounds of the composition SnR_2O, inasmuch as it was readily soluble in many organic solvents, such as benzene, ethyl acetate, chloroform, or carbon tetrachloride; from its solutions in all these and in several other organic liquids, it separated in well-defined, square tablets, which contained solvent, and which, when freed from the latter, melted at about 254—260°. The quantity of solvent in the crystals deposited from the four liquids just named could be expressed in certain molecular proportions (p. 2043).

Numerous analyses of the recrystallised, solvent-free substance gave results which showed clearly that the compound was not the dihydroxy-derivative $Sn(CH_2Ph)_2(OH)_2$, but which agreed with those required by a condensation product of the latter, having the formula:

$$HO{\cdot}Sn(CH_2Ph)_2{\cdot}O{\cdot}Sn(CH_2Ph)_2{\cdot}O{\cdot}Sn(CH_2Ph)_2{\cdot}OH.$$

As, however, the compositions of successive condensation products differ but little from one another, and gradually approach very closely to that of the oxide, $Sn(CH_2Ph)_2O$, the analytical results were not so conclusive as might have been desired.

Molecular-weight determinations by the cryoscopic method in benzene solution and also by the ebullioscopic method in chloroform solution, gave fairly concordant values of about 2700; these

gree with that required by a condensation product formed from , or 9 molecules of dihydroxydibenzylstannane, with elimination f 7 or 8 molecules of water respectively. The question arises, herefore, what weight is to be attached to these results?

Now in the case of the open-chain condensation products of iphenylsilicanediol, namely, anhydrobis- and dianhydrotris-iphenylsilicanediol, in both of which there is some independent vidence to confirm the result of the molecular-weight determina-ions (Kipping, T., 1912, **101**, 2125), the average experimental alue obtained in benzene solution was ouly about 30 per cent. igher than the calculated value; if, therefore, analogy is a safe uide in the present instance, it would seem that the results btained in the case of the tin compound are also to be trusted.

This, however, is a new type of tin compound, and molecular-eight determinations with tin derivatives of even an approxi-nately similar nature have not yet been published. We therefore xamined dibenzylstannic acetate and tribenzylstannol,

$$Sn(CH_2Ph)_3{\cdot}OH,$$

n benzene solution, and found that whereas the experimental esults agreed with the theoretical value in the case of the former, hey were very much too high in that of the latter. The fact that his relatively simple monohydroxy-derivative is so largely asso-iated in benzene solution renders it very probable that a dihydroxy-ompound of the constitution:

$$HO{\cdot}Sn(CH_2Ph)_2{\cdot}O{\cdot}Sn(CH_2Ph)_2{\cdot}O{\cdot}Sn(CH_2Ph)_2{\cdot}OH$$

would exhibit a similar behaviour; for this and other reasons the esults of the analyses of the condensation product are clearly of uch greater importance than those of the molecular-weight deter-ninations.

It may therefore be concluded that the tin compound in question as the constitution just given, and is an analogue of dianhydro-risdiphenylsilicanediol; in accordance with this view it is named *ianhydrotrisdibenzylstannanediol.*

Although there may still be some doubt as to the constitution f the compound, we believe that there is conclusive evidence that t is an open-chain condensation product of dihydroxydibenzyl-tannane, and that the only point which is not quite decided is he number of molecules of the dihydroxy-compound which have ondensed together.

This evidence is afforded by the behaviour of the compound hen it is heated and when it is treated with a solution of otassium hydroxide. When heated alone at about 150—170°, r in boiling bromobenzene solution, it is converted with loss of he elements of water into an oxide, $[Sn(CH_2Ph)_2O]_n$, which, like

all the compounds of this type, is insoluble in all ordinary organic solvents, even in those of high boiling point.

Some attempts were made to determine the quantity of water formed during this transformation, but at the temperature required to bring about the conversion, dianhydrotrisdibenzylstannanediol is readily oxidised, with the formation of benzaldehyde and dibenzyl, and even when it is heated in an atmosphere of carbon dioxide traces of these compounds are formed; apparently also a small proportion of the original substance is decomposed by the water which is formed during its conversion into the oxide, toluene being evolved. For these reasons the determinations were only approximately correct, and although the results agreed fairly well with those required for the conversion of a dianhydrobisdibenzylstannanediol into the corresponding oxide, they were not altogether satisfactory.

The insoluble oxide is also produced when the open-chain compound is left for some time in contact with a moderately concentrated solution of potassium hydroxide; further, it is deposited as a powder, together with dianhydrotrisdibenzylstannanediol, when a solution of the potassium derivative referred to above, in excess of potassium hydroxide solution, is kept for some days at the ordinary temperature in absence of air; also when dichlorodibenzylstannane is warmed with a concentrated solution of ammonium hydroxide.

All these methods of formation are analogous to those by which trianhydrotris- and tetra-anhydrotetrakis-diphenylsilicanediol are produced from the open-chain condensation products of diphenylsilicanediol (Kipping, T., 1912, **101**, 2136, 2138).

The oxide, $[Sn(CH_2Ph)_2O]_n$, melts and decomposes at 254—260°, that is to say, at the same temperature as the open-chain compound, which obviously is converted into the oxide below its melting point. The only evidence available on which to judge of the molecular formula of the oxide being its formation from the open-chain compound, it seems very probable that the oxide is a closed-chain condensation product of the following character:

$$O{<}{\genfrac{}{}{0pt}{}{Sn(CH_2Ph)_2\cdot O}{Sn(CH_2Ph)_2\cdot O}}{>}Sn(CH_2Ph)_2.$$

At the same time it is not impossible that two (or more) molecules of the hydroxy-compound condense together to give a product containing a closed chain of six tin atoms and six oxygen atoms.

Attempts to find a solvent for the oxide led to the discovery that the compound is readily acted on by boiling quinoline, giving a brown solution; from this solution a very small proportion of

ianhydrotrisdibenzylstannanediol and a little tribenzylstannanol ere isolated, but the main product was a resin, which yielded ichlorodibenzylstannane with acetone and hydrochloric acid.

A very small proportion of tribenzylstannanol is also formed hen dianhydrotrisdibenzylstannanediol is heated alone at about 60° in an atmosphere of carbon dioxide, or with water at 180°. t is obvious from these and other instances that the hydrocarbon adicles attached to the tin atom are highly mobile; dichloro-iphenylstannane, for example, gives triphenylstannic chloride hen it is merely treated with sodium amalgam or with a solution f ammonium hydroxide (Aronheim, *Annalen*, 1878, **194**, 145), nd the compound $CH_2 \cdot SnO_2K$ gives $[(CH_3)_2SnO]_n$ when it is warmed with alcoholic potash (Meyer, *Ber.*, 1883, **16**, 1442).

Experiments on the hydrolysis of dichlorodiphenylstannane and ichlorodi-*p*-tolylstannane failed to give a soluble compound analo-ous to dianhydrotrisdibenzylstannanediol; the only product in ach case was a powder insoluble in all the neutral solvents which ere tried, and having the composition of the oxide.

The results described in this paper point decidedly to the conclu-ion that dibenzylstannic oxide is a closed-chain compound of the olecular formula $[Sn(CH_2Ph)_2O]_n$, where $n=3$ or some multiple f 3. From analogy it may be inferred that all the other dialkyl r diaryl stannic oxides have a similar constitution. Further, our esults afford some experimental evidence in favour of the view hat the acids supposed to have the composition H_2SnO_3 are highly omplex condensation products of stannic hydroxide, $Sn(OH)_4$, or re mixtures of such compounds, and that the relationship between he preparations usually known as the α- and the β-acids may be omewhat analogous to that between dianhydrotrisdibenzyl-annanediol and dibenzylstannic oxide.

EXPERIMENTAL.

Hydrolysis of Dibenzyldichlorostannane.

When finely-divided dibenzyldichlorostannane (Smith and pping, T., 1912, **101**, 2553) is left in contact with a cold aqueous ution of potassium hydroxide, it gradually disappears, giving a luble product, which is doubtless a potassium derivative, $n(CH_2 \cdot C_6H_5)_2(OK)_2$ or $Sn(CH_2 \cdot C_6H_5)_2(OK)(OH)$. An approxi-ately 7 per cent. solution of the alkali hydroxide seems to give the st results; when more concentrated solutions are used, the soluble tassium derivative which is first formed undergoes decomposition, insoluble powder being deposited (see below).

From the clear alkaline solution, carbonic acid precipitates a ourless, somewhat flocculent solid, which, *immediately* after its

formation, is rapidly dissolved by a 7 per cent. solution of potassium hydroxide. This precipitate seems to undergo quickly some progressive change; thus, by the time it has been separated by filtration, and washed by the aid of the pump, it has altered to such an extent that it is only very slowly acted on by the alkali, and when it has been air-dried it is even more slowly attacked. Comparative experiments, under similar conditions, showed that freshly prepared, washed samples (about thirty minutes old), left in contact with a 5 per cent. potassium hydroxide solution, disappeared at the end of the second day, whilst the air-dried samples required about twenty-four hours longer.

A substance, apparently identical with that just described, is precipitated when the alkaline solution of the potassium derivative is cautiously treated with dilute acetic acid in quantity insufficient for neutralisation; also when finely-divided dibenzyldichlorostannane is triturated with a cold dilute aqueous solution of ammonium hydroxide, fresh quantities of the solution being added to the product until the latter is free from halogen.

Dianhydrotrisdibenzylstannanediol,

$$HO{\cdot}Sn(CH_2Ph)_2{\cdot}O{\cdot}Sn(CH_2Ph)_2{\cdot}O{\cdot}Sn(CH_2Ph)_2{\cdot}OH.$$

The product, obtained by any of the three methods just described, washed with water, and roughly dried on porous earthenware, sinters at about 100°, and melts at about 250—260°, turning slightly brown; when washed with cold ether, which removes a small quantity of some resinous matter, the sample does not sinter at 100°, but melts at the same temperature as before; the sintering, therefore, is doubtless due to the presence of this resinous impurity and not to the loss of the elements of water. The impurity in question is probably some product of atmospheric oxidation, as the originally colourless precipitate turns yellow superficially on exposure to the air. The air-dried precipitate, freed from the small proportion of resinous matter with the aid of ether or acetone, dissolves freely in cold benzene; when the solution is evaporated at the ordinary temperature, it deposits large, thick, square plates which contain solvent, but which rapidly lose it on exposure to the air, giving a colourless powder; the latter melts at 254—260°, decomposing slightly, but, unlike the very finely-divided product obtained by precipitation, it does not seem to undergo atmospheric oxidation.

The following preparations of this compound were analysed, some having been obtained by methods described later:

I. and II. Different samples precipitated from alkaline solution

ith carbonic acid, recrystallised from benzene, and kept in a acuum until constant in weight.

III. A similar sample, which was washed with alcohol repeatedly iter it had been crystallised from benzene.

IV. and V. Samples prepared by decomposing dichlorodibenzyl-annanediol with ammonium hydroxide solution, crystallising om benzene, etc.

VI. Sample deposited from a solution in potassium hydroxide, ystallised from benzene, etc. (p. 2047).

I.	0·2520	gave	0·4753 CO_2	and 0·1008 H_2O.	C=51·5;	H=4·5.
II.	0·2013	,,	0·3818 CO_2	,, 0·0822 H_2O.	C=51·8;	H=4·5.
III.	0·1549	,,	0·2946 CO_2	,, 0·0635 H_2O.	C=51·9;	H=4·5.
IV.	0·2173	,,	0·4133 CO_2	,, 0·0871 H_2O.	C=51·4;	H=4·4.
V.	0·1602	,,	0·3029 CO_2	,, 0·0644 H_2O.	C=51·7;	H=4·5.
IV.	0·1851	,,	0·3506 CO_2	,, 0·0746 H_2O.	C=51·6;	H=4·5.

$C_{42}H_{44}O_4Sn_3$ requires C=51·9; H=4·6 per cent.

As the dihydroxy-derivative would contain 50·1 per cent. of arbon and 4·8 per cent. of hydrogen, whereas the oxide would ontain 52·9 per cent. of carbon and 4·4 per cent. of hydrogen, t is obvious that the compound prepared by the above-described ethods is neither of these substances. The average results agree est with those required by an open-chain condensation product ormed from 3 molecules of dibenzylstannanediol with elimination f 2 molecules of water, but allowing for the usual experimental rror, they would also agree passably with those required by the ext higher condensation product of the same type.

The molecular weight of various preparations was determined in enzene solution by the cryoscopic method.

Substance. Grams.	Solvent. Grams.	Δt.	M.W.
0·511	14·8	0·062	2481
0·543	14·6	0·075	2482
0·563	14·8	0·077	2802
0·962	14·8	0·127	2562
0·975	14·6	0·130	2568
1·481	13·4	0·208	2666
1·635	14·8	0·185	2994

he compound is so sparingly soluble in cold phenol that this ent could not be employed, but some determinations were made the ebullioscopic method in chloroform solution.

Substance. Gram.	Solvent. c.c.	Δt.	M.W.
0·753	7·1	0·098	2811
0·753	7·9	0·088	2816
0·753	8·6	0·081	2806
0·753	9·1	0·073	2947

As the molecular weight of a dianhydrotrisdibenzylstannanediol

is only 969, experiments were made with dibenzylstannic acetate and also with tribenzylstannanol in benzene and in chloroform solutions in order to test the validity of the above results.

The acetate was examined by the cryoscopic method:

Substance. Gram.	Benzene. Grams.	Δt.	M.W.
0·225	12·4	0·203	427
0·488	12·4	0·405	487
0·684	12·4	0·545	505

The calculated molecular weight is 419.

The tribenzylstannanol was examined by the cryoscopic and by the ebullioscopic methods:

Substance. Gram.	Benzene. Grams.	Δt.	M.W.
0·257	17·7	0·110	660

Substance. Gram.	Chloroform. c.c.	Δt.	M.W.
0·314	6·4	0·162	786
0·314	7·3	0·144	784
0·314	8·6	0·125	759
0·314	9·5	0·102	841
0·992	9·7	0·367	727
0·992	10·4	0·32	775
0·992	10·7	0·297	813
0·992	11·3	0·280	821
0·992	11·7	0·269	813

The calculated value for the molecular weight is 409.

In view of the very high results obtained with the monohydroxy-derivative, it would seem that a dihydroxy-compound of the constitution of dianhydrotrisdibenzylstannanediol might also give a very abnormal value; for this and other reasons it may be inferred that the condensation product described above has the constitution assigned to it, and that the molecular-weight determinations indicate association due to the presence of the two hydroxyl groups.

Dianhydrotrisdibenzylstannanediol is very readily soluble in benzene, chloroform, or carbon tetrachloride, and dissolves freely in ethyl acetate, but is only sparingly soluble in cold ether or acetone, practically insoluble in alcohol or light petroleum, and insoluble in water. From the first four solvents just mentioned, and also from ethyl bromide or bromobenzene, the compound is deposited in crystals which contain solvent. All these crystals lose their solvent so rapidly on exposure to the air, even at the ordinary temperature, that the determination of their composition presents some difficulty, more especially when the crystals are small, as are those obtained from ethyl acetate and carbon tetrachloride solutions. In the case of these solvents, the freshly prepared crystals were rapidly pressed between layers of filter paper, placed in a weighing bottle, and weighed at intervals of about five minutes.

At first the loss in weight was very rapid, but as soon as the adherent solvent had evaporated, the rate of loss suddenly diminished, and the weight of the preparation at this break was taken to be that of the solvent-containing crystals. The samples were then kept under greatly diminished pressure; as the last traces of solvent were lost only very slowly, one or two days elapsed before a constant weight was reached.

Crystals from benzene: 0·684 lost 0·0833 or 12·2 per cent.

$3C_{42}H_{44}O_4Sn_3,5C_6H_6$ requires 12·0 per cent.

Crystals from ethyl acetate: 1·207 lost 0·1162 or 9·98 per cent.

$3C_{42}H_{44}O_4Sn_3,4CH_3{\cdot}CO_2Et$ requires 10·7 per cent.

Crystals from chloroform: 0·852 lost 0·1536 or 17·9 per cent.

$3C_{42}H_{44}O_4Sn_3,5CHCl_3$ requires 17·3 per cent.

Crystals from carbon tetrachloride: 0·920 lost 0·1567 or 17·0 per cent.

$3C_{42}H_{44}O_4Sn_3,4CCl_4$ requires 16·9 per cent.

For the reason stated above, these results are not very trustworthy, and although the compositions of the various solvent-containing crystals are expressed by the above molecular proportions, others are not excluded.

Atmospheric Oxidation of Dianhydrotrisdibenzylstannanediol.

As some of the open-chain condensation products of diphenylsilicanediol and of dibenzylsilicanediol lose the elements of water and are converted into closed-chain condensation products when they are heated alone at a sufficiently high temperature, it seemed probable that dianhydrotrisdibenzylstannanediol would undergo a similar transformation; moreover, if the quantity of water formed in this process could be accurately determined, the results would afford evidence as to the constitution of the original substance.

Now when dianhydrotrisdibenzylstannanediol, crystallised from benzene and freed from solvent in a vacuum, is heated in the air at 100°, although it loses in weight, the loss is far greater than it would be if it were due to the elimination of water; thus at the end of two hours' heating, the loss amounted to 2·9 per cent.; at the end of a further six hours it was 6·4 per cent., and after six hours more 8·3 per cent. Even then there was no approach to a constant weight, and although the substance had turned brown and some of it had decomposed, it had not been converted into the closed-chain compound.

The loss in weight seems, in fact, to be entirely due to atmospheric oxidation, which results in the formation and subsequent volatilisation of benzaldehyde and dibenzyl; if the heating is carried out at about 115° in a glass tube, oily drops, smelling

strongly of benzaldehyde, are deposited on the colder portions of the glass.

When the freshly-crystallised compound is freed from solvent and heated at 100° in a stream of dried carbon dioxide, the loss in weight is practically negligible; if, however, the same sample is again heated (after it has been exposed to the air) a decrease of weight of something like 0·1 per cent. is observed, and losses of about the same amount continue to occur after each heating. As this loss is approximately the same each time, and does not vary appreciably and regularly with the period of heating, it is in all probability due to the effect of traces of oxygen, most of which are probably absorbed by the powder during its exposure to the air in the operation of weighing, etc.

Conversion of Dianhydrotrisdibenzylstannanediol into the Oxide.

When a weighed quantity of pure dianhydrotrisdibenzylstannanediol is heated at 100° in an atmosphere of dried carbon dioxide, a calcium chloride tube attached to the apparatus does not increase in weight appreciably, even after the substance has been heated during two hours. If then the temperature is raised to about 160° and kept between 160° and 170° for about an hour, water is evolved, and the increase in weight of the calcium chloride tube amounts to about 1·7 per cent. of the weight of the original substance; further, at this stage the soluble compound has been almost entirely transformed into a powder, which is insoluble in benzene. A further increase in weight of the calcium chloride tube (about 0·1 per cent. of the weight of the original substance) is observed if the temperature is then raised to and kept at 170—175° during about four hours, but this increase is probably not due to absorption of water.

It was thus proved that dianhydrotrisdibenzylstannanediol undergoes a profound change at about 160° with liberation of water.

Unfortunately, the quantity of water evolved during this transformation could not be accurately determined, owing to the fact that towards the end of the operation, traces of oily products, as well as water, collect in the calcium chloride tube. So far as could be determined, the quantity was approximately 1·8 per cent. of the weight of the substance taken; at any rate, it did not exceed 2 per cent. As this loss corresponds approximately with the quantity, namely, 1·85 per cent., which would be formed in the conversion of a dianhydrotrisdibenzylstannanediol into the corresponding oxide, the results of these experiments seem to confirm the analytical data, and to show that the substance has the constitution suggested.

Among the oily products collected in the calcium chloride tube, ibenzyl was identified, but doubtless the oil also contains benz-ldehyde, and possibly toluene. These products seem to result from he action of traces of atmospheric oxygen, which it is practically mpossible to exclude, and also from that of the water which is ormed during the transformation of the soluble compound into he insoluble oxide; when it is borne in mind that 1 gram of oxygen night give rise to the formation of more than 11 grams of dibenzyl, nd that the total gain in weight of the calcium chloride tube n the experiments just described is only about 0·03—0·04 gram, t is obvious that a minute quantity of oxygen might vitiate the esults.

Action of Water on Dianhydrotrisdibenzylstannanediol.

In order to test the conclusion that the oily products obtained in he above-described experiments are formed, at any rate in part, y the action of the liberated water on dihydrotrisdibenzylstannane-liol. some of this substance was heated with water and a little cetone at 180° during eight hours in a sealed tube. The substance ad changed into a brown resin, and seemed to be completely lecomposed. The contents of the tube were oily, and had a ronounced odour of toluene; from the brown resin, which was ompletely soluble in ether, and therefore free from stannic oxide, small proportion of dibenzyl and a considerable proportion of ribenzylstannanol were isolated; the presence of dianhydrotris-ibenzylstannanediol in this product could not be established.

Dibenzylstannic Oxide, $[Sn(CH_2Ph)_2O]_n$.

The compound obtained by heating dianhydrotrisdibenzylstan-anediol alone, as described above, is not quite pure; it contains, t any rate in some instances, a relatively small proportion of ribenzylstannanol, which may be extracted with boiling benzene. he residue then consists of a practically colourless powder, which insoluble in benzene and in all the common solvents. A sample as analysed with the following result:

0·1860 gave 0·3538 CO_2 and 0·0737 H_2O. C=51·9; H=4·4.

$C_{14}H_{14}OSn$ requires C=53·0; H=4·45 per cent.

This and other analyses show that the substance has the com-osition of a dibenzylstannic oxide; on treatment with a solution hydrochloric acid in acetone, it is converted, apparently quanti-tively, into dichlorodibenzylstannane.

From its method of formation, and for various other reasons, would seem highly probable that this oxide is a closed-chain

compound, the molecule of which contains at least three atoms of tin.

The oxide turns yellow superficially on exposure to light and air, and when heated in the air at about 115° it undergoes oxidation, giving an oil, which smells strongly of benzaldehyde.

Conversion of Dianhydrotrisdibenzylstannanediol into the Oxide, $[Sn(CH_2Ph)_2O]_n$, in Bromobenzene Solution.

As the soluble hydroxy-compound is converted into the insoluble oxide when it is heated alone at about 150—160°, it seemed probable that this change might also be brought about by heating a solution of the substance in some inert solvent; experiment showed that this inference was well founded.

Dianhydrotrisdibenzylstannanediol dissolves freely in cold bromobenzene, and when the solution is allowed to evaporate spontaneously it deposits colourless tablets, which contain solvent and effloresce on exposure to the air. When, however, the solution is heated at its boiling point on a reflux apparatus, it begins to deposit a colourless powder after a short time, and in the course of about half an hour practically nothing remains in solution.

This powder is insoluble in all the common solvents, and melts at 254—260°; when treated with acetone and hydrochloric acid it gives dibenzylstannic chloride, apparently as the sole product. So far as could be ascertained, it was identical with the oxide prepared by heating dianhydrotrisdibenzylstannanediol alone, and an analysis of it gave the following result:

0·1815 gave 0·3494 CO_2 and 0·0721 H_2O. C=52·43; H=4·41.

$C_{14}H_{14}OSn$ requires C=53·0; H=4·45 per cent.

Action of Potassium Hydroxide Solution on Dianhydrotrisdibenzylstannanediol.

When dianhydrotrisdibenzylstannanediol is left in contact with a 15 per cent. solution of potassium hydroxide during some three days, a small proportion of it dissolves. The residue no longer consists entirely of the original substance; when washed, dried, and treated with benzene, a part of it dissolves, and the solution gives crystals of dianhydrotrisdibenzylstannanediol when it is allowed to evaporate. The insoluble portion melts at 254—260°, gives dichlorodibenzylstannane with acetone and hydrochloric acid and is apparently identical with the insoluble oxide obtained by the other methods described above. A sample of the washed insoluble product was analysed; the result was, however, not very satisfactory, possibly owing to the presence of occluded alkali:

0·1629 gave 0·3214 CO_2 and 0·0665 H_2O. C=51·8; H=4·3.

$C_{14}H_{14}OSn$ requires C=53·0; H=4·45 per cent.

The filtered potassium hydroxide solution slowly deposits a colourless powder when it is kept out of contact with the air, but even at the end of several days only a small proportion of the dissolved matter has been precipitated. The precipitate consists of a mixture of dianhydrotrisdibenzylstannanediol and the insoluble oxide, which may be separated from one another in the usual manner.

The above-described alkaline solution, which doubtless contains the potassium derivative of dibenzylstannanediol, behaves in a manner analogous to that of an alkaline solution of diphenylsilicanediol; in both cases a mixture of condensation products of the diol is slowly deposited from the solution.

The insoluble oxide is also formed when dichlorodibenzylstannane is warmed with a concentrated aqueous solution of ammonium hydroxide; the colourless powder which is thus produced contains a small proportion of dianhydrotrisdibenzylstannanediol, which is easily removed with the aid of benzene.

The insoluble oxide may be partly transformed into dianhydrotrisdibenzylstannanediol with the aid of a 15 per cent. solution of potassium hydroxide; when left in contact with such a solution during some days, a small proportion dissolves, and from the filtered liquid dianhydrotrisdibenzylstannanediol is precipitated on treatment with carbon dioxide.

Action of Boiling Quinoline on the Oxide.

When the insoluble oxide is boiled with quinoline, it disappears in the course of about ten minutes, giving a solution which is slightly coloured. If the quinoline is then separated by distillation in steam, there remains a solid residue, which is soluble in benzene. The benzene solution deposits crystals, melting at 124—125°, which were identified as those of tribenzylstannanol; on treatment with acetyl chloride they gave tribenzylstannic chloride. The benzene mother liquors, when diluted with light petroleum, gave a precipitate, from which a little dianhydrotrisdibenzylstannanediol was isolated after prolonged fractional crystallisation, but the main product was a resin, which gave impure dichlorodibenzylstannane on treatment with acetone and hydrochloric acid.

Action of Boiling Benzyl Acetate on the Oxide.

Boiling benzyl acetate attacks the insoluble oxide, and after a very short time a colourless solution is obtained; if the solvent is then separated by distillation in steam, there remains a colourless solid, which dissolves freely in benzene. This solution deposits a finely crystalline powder, which melts at about 155—170°,

apparently without decomposing, and the melting point does not undergo any alteration, even after repeated crystallisation from benzene or from mixtures of acetone and benzene. On treatment with alcoholic hydrochloric acid, this substance gave dichlorodibenzylstannane:

0·2422 gave 0·4581 CO_2 and 0·1007 H_2O. C=51·6; H=4·6.
0·1813 „ 0·3426 CO_2 „ 0·0762 H_2O. C=51·5; H=4·6.
$C_{18}H_{20}O_4Sn$ requires C=51·5; H=4·8 per cent.

Although these percentages agree closely with those required by dibenzylstannic acetate, $Sn(CH_2Ph)_2(OAc)_2$, the last-named compound melts at 136—137°, and is different in other respects from the compound melting over the wide range given above. The results agree moderately well with those required by a hydroxyacetate derived from dianhydrotrisdibenzylstannanediol, and having the constitution:

$HO{\cdot}Sn(CH_2Ph)_2{\cdot}O{\cdot}Sn(CH_2Ph)_2{\cdot}O{\cdot}Sn(CH_2Ph)_2{\cdot}OAc$,

as such a compound would contain 52·2 per cent. of carbon and 4·5 per cent. of hydrogen. As, however, the melting point was so very indefinite, the apparently homogeneous substance may have been a mixture; it was not further examined.

Diphenylstannic Oxide, $[SnPh_2O]_n$.

Diphenylstannic oxide has been prepared and examined by Aronheim (*Annalen*, 1878, **194**, 145), who obtained it by decomposing dichlorodiphenylstannane with alkalis; as it seemed possible that under suitable conditions the dichloride might give a condensation product analogous to dianhydrotrisdibenzylstannanediol, we made some experiments in this direction.

In the first place, tetraphenylstannane was prepared by the process employed by Pfeiffer and Schnurmann (*Ber.*, 1904, 37, 321), and this compound was then converted into dibromodiphenylstannane by treatment with bromine according to a method described by Polis, which we carried out as follows: Tetraphenylstannane (1 mol.) is suspended in dry carbon tetrachloride, in which it is only sparingly soluble; the liquid is heated under a reflux apparatus, and bromine (2 mols.), mixed with carbon tetrachloride, is then slowly dropped down the condenser. At first the reaction takes place very rapidly, and the colour of the halogen disappears at once, but when nearly all the bromine has been added, the solution remains reddish-brown, even after it has been boiled for some time. When the reaction is at an end, the solution, which is quite free from suspended tetraphenylstannane, is submitted to distillation in steam in order to remove the carbon tetrachloride and bromobenzene. The tin compound which remains is treated with

solution of sodium hydroxide, and the resulting oxide is separated by the aid of the pump, and washed with alcohol and ether. The product is then converted into dichlorodiphenylstannane by treatment with alcohol and hydrochloric acid.

The dichloride, purified by recrystallisation from alcohol, was cautiously hydrolysed with an ice-cold dilute solution of potassium hydroxide. It was thereby converted into a colourless powder, and the alkaline liquid, separated by filtration, gave no precipitate when treated with excess of carbon dioxide. In other experiments an alcoholic solution of the dichloride was slowly dropped into excess of an ice-cold, well-stirred, dilute aqueous solution of ammonium hydroxide; the product, so far as could be ascertained, was identical with that obtained by the first method, and it was insoluble in all the ordinary solvents.

This oxide, unlike the corresponding dibenzyl derivative, seems to be quite unchanged when it is left in contact with a 15 per cent. solution of potassium hydroxide, a fact which is the more noteworthy since phenyl derivatives are, as a rule, so much more strongly acidic than benzyl derivatives of similar constitution.

The diphenylstannic oxide was also unchanged when it was boiled with quinoline during some time.

Dichlorodi-p-*tolylstannane*, $Sn(C_6H_4Me)_2Cl_2$.

This dichloride was prepared by methods analogous to those used in the case of the corresponding diphenyl derivative, starting with tetra-*p*-tolylstannane, which has been described by Pfeiffer (*Zeitsch. anorg. Chem.*, 1910, **68**, 102). The tetratolyl compound having been treated with bromine (2 mols.) in boiling carbon tetrachloride solution, the solvent and the bromotoluene were separated by distillation in steam, and the remaining tin compound was treated with excess of a solution of sodium hydroxide. The washed and dried oxide was first boiled with benzene in order to remove any unchanged tetratolylstannane, and then converted into the dichloride by treatment with alcohol and hydrochloric acid.

The alcohol was then evaporated, and the dichloride extracted with light petroleum; from this solution it was deposited in colourless plates, which were purified by recrystallisation from the same solvent:

0·4960 gave 0·3771 AgCl. Cl = 18·8.

$C_{14}H_{14}Cl_2Sn$ requires Cl = 19·1 per cent.

Dichlorodi-p-*tolylstannane*, like the corresponding diphenyl compound, is very readily soluble in all the ordinary organic solvents, but it crystallises well from light petroleum; it melts at 38—40°.

Di-p-tolylstannic Oxide, $[Sn(C_6H_4Me)_2O]_n$.

The hydrolysis of the dichloride was carried out with a solution of potassium hydroxide and with ammonium hydroxide, exactly as described in the case of the diphenyl derivative; the only product which was thus obtained was a colourless solid, which did not melt at 300°, was insoluble in all the common solvents, and was reconverted into the dichloride on treatment with alcoholic hydrochloric acid:

0·1670 gave 0·3252 CO_2 and 0·0669 H_2O. C=53·1; H=4·45.

$C_{14}H_{14}OSn$ requires C=52·9; H=4·4 per cent.

These results seem to show that the dibenzyl compound which we have described as dianhydrotrisdibenzylstannanediol has no analogue in the diphenyl and di-*p*-tolyl series; there is every reason to believe, however, that the diphenyl- and the di-*p*-tolyl-stannic oxides, like the corresponding dibenzyl compound, are closed-chain condensation products of the respective dihydroxy-compounds.

The authors desire to acknowledge their indebtedness to the Government Grant Committee of the Royal Society for a grant in aid of this research.

UNIVERSITY COLLEGE,
NOTTINGHAM.

CCXVII.—*Some Derivatives of Oleanol.*

By FRANK TUTIN and WILLIAM JOHNSON SMITH NAUNTON.

IN a former communication (T., 1908, **93**, 896) Dr. Power and one of us described the isolation from olive leaves of a crystalline substance, which was designated oleanol. It was shown that oleanol possessed the formula $C_{31}H_{50}O_3$, and that it contained two hydroxyl groups, one of which had phenolic properties. Thus, on methylation with methyl iodide and sodium ethoxide, oleanol yielded a monomethyl derivative, and the latter, on acetylation, gave a monoacetyl compound. Oleanol itself was shown to afford a diacetyl derivative, which, on heating with dilute alcohol, lost one acetyl group, yielding monoacetyloleanol.

It was also shown (*loc. cit.*) that when diacetyloleanol (m. p. 208°) is heated above its melting point it underwent some change, gas being evolved, and a compound formed which did not melt at 310°. The analysis of the latter compound indicated it to possess the formula $C_{31}H_{48}O_3$, and, since it was not affected by alkalis, it

is concluded that it had been formed by the elimination of the o acetyl groups from diacetyloleanol.

More recently, Power and Moore (T., 1910, **97**, 1104) isolated rom the leaves of *Prunus serotina* a substance isomeric with eanol. This compound, which was strictly analogous to oleanol its properties, was designated prunol. Diacetylprunol, on heating, nderwent a change similar to that suffered by diacetyloleanol, but this case it was conclusively shown that the reaction consisted the elimination of one molecule of acetic anhydride from two olecules of the diacetyl compound. The product of high melting int (315°) has the composition $C_{66}H_{102}O_7$, but, since it is not fected by heating with alcoholic potassium hydroxide, it is probble that some change had occurred other than the condensation nsequent upon the elimination of acetic anhydride.

A quantity of the alcoholic extract of olive leaves being available, it was considered of interest to pursue the investigation of leanol with the hope of throwing some light on its constitution, nd also to ascertain whether the behaviour of the diacetyl derivtive on heating was analogous to that of diacetylprunol.

Although the amount of oleanol available did not permit of uch information being gained regarding the constitution of a bstance of so large a formula, a number of interesting derivatives ave been prepared from it.

With regard to the change suffered by the diacetyl derivative on eating, it has now been ascertained that this reaction proceeds nalogously to that undergone by diacetylprunol, and results in the rmation of a substance possessing the formula $C_{66}H_{102}O_7$. The sleading analytical results previously obtained by Power and utin have been found to be due to the persistent retention of nzene, which was employed for the crystallisation of the comund in question.

When oleanol, $C_{31}H_{50}O_3$, is oxidised with potassium permannate in acetic acid solution it yields a dihydroxy-compound having he formula $C_{29}H_{46}O_4$. It would appear, therefore, that oleanol ontains the group $CH_3{\cdot}CH{:}C{<}$, and that this undergoes oxidation, ielding acetic acid and a ketone. Although no direct evidence f the ketonic character of the substance $C_{29}H_{46}O_4$ was obtained, t would appear certain that it contains a carbonyl group, and it is roposed to designate it *oleanone*. It yields *mono-* and *di-acetyl* erivatives.

The reactions which ensued on heating oleanone and diacetyleanone with acetic acid containing water and hydrochloric acid espectively were of an unexpected nature, and serve to explain he considerable difficulty which was at first experienced in preparng any appreciable quantity of the first-mentioned compound.

Oleanone, when heated with glacial acetic acid, undergoes no change, but if the acid is slightly diluted with water a pink colour rapidly develops, which changes, first to green, and then to a dark violet colour, the latter gradually fading. On removal of the acetic acid a product is obtained which is uncrystallisable, but yields a crystalline *acetyl* derivative having the formula

$$C_{50}H_{76}O_7 \cdot CO \cdot CH_3.$$

On hydrolysis, the latter yields the corresponding *alcohol*, $C_{50}H_{76}O_5(OH)_2$. This change may be accounted for, empirically, by the condensation of 2 molecules of oleanone, accompanied by the addition of one molecule of water and the elimination of the elements $C_8H_{16}O_2$:

$$2C_{29}H_{46}O_4 + H_2O = C_{50}H_{78}O_7 + C_8H_{16}O_2.$$

There are several ways possible in which such a change could occur, but the amount of material available was not sufficient to permit of the determination of the exact course of the reaction.

The above-described reaction is of interest inasmuch as the changes of colour closely resemble those produced by a phytosterol when treated with a drop of sulphuric acid in the presence of acetic anhydride. It is possible, therefore, that some similar condensation may take place in the case of the phytosterols.

When diacetyloleanone is heated with acetic acid containing aqueous hydrochloric acid, an analogous reaction occurs. The same change of colours takes place, and a *compound*, $C_{50}H_{77}O_7 \cdot CO \cdot CH_3$, results. The latter proved to be the monoacetyl compound corresponding with the above-mentioned diacetyl derivative,

$$C_{50}H_{76}O_7(CO \cdot CH_3)_2.$$

On acetylation it yielded the latter, and on hydrolysis with alkali it gave the dihydroxy-compound, $C_{50}H_{76}O_5(OH)_2$. These changes may be represented as follows:

$$\begin{tikzcd}
C_{29}H_{46}O_4 \arrow[r, "Ac_2O"] \arrow[d, "H_2O"] & C_{29}H_{44}O_4Ac_2 \arrow[r, "HCl+H_2O"] & C_{50}H_{77}O_7Ac \arrow[d, "KOH"] \arrow[dl, "Ac_2O"'] \\
{[C_{50}H_{78}O_7]} \arrow[r, "Ac_2O"] & C_{50}H_{76}O_7Ac_2 \arrow[r, shift left, "KOH"] & C_{50}H_{76}O_5(OH)_2 \arrow[l, shift left, "Ac_2O"]
\end{tikzcd}$$

The further oxidation of oleanone, $C_{29}H_{46}O_4$, could not be effected by means of potassium permanganate, and recourse was therefore had to the use of chromic acid. This resulted in the formation of a *substance*, $C_{29}H_{42}O_4$, and, since the latter yields only a *monoacetyl* derivative, it would appear that the alcoholic hydroxyl group originally present in oleanol had been oxidised to a keto-group. The other two atoms of hydrogen removed are possibly accounted

by the oxidation of a reduced aromatic nucleus. When the bstance, $C_{29}H_{42}O_4$, which melts at 275°, was submitted to the irly prolonged action of alcoholic potassium hydroxide it was nverted into an isomeride, melting at 315°. If, however, the tion of the alkali was still more prolonged further, and more ofound, changes occurred.

The direct oxidation of oleanol by means of a warm solution of romic acid in acetic acid resulted in the formation of the above-entioned compound, $C_{29}H_{42}O_4$, together with a mixture of carb-ylic acids. It was ascertained that the latter contained at least ree compounds, but no crystalline acid could be isolated from it.

Experimental.

The alcoholic extract of olive leaves from which the oleanol was tained was the same as that employed for the investigation of e constituents of olive leaves (T., 1908, **93**, 891). It was mixed th water and distilled in a current of steam for the removal the volatile constituents, after which the resin was separated om the aqueous liquid. The resin was then mixed with purified wdust, and the thoroughly dried mixture extracted, first with troleum (b. p. 35—50°), and then with ether. The ether extract nsisted largely of crude oleanol, which separated as a green, aringly soluble powder. The latter was collected, and crystallised om alcohol with the employment of animal charcoal, when pure eanol was obtained in slender, colourless crystals, melting at °. The mother liquors from this substance gave further ounts of oleanol in an impure, amorphous condition, from which e pure compound was obtained by means of the acetyl derivative. e latter, on treatment with alcoholic potassium hydroxide, yielded re oleanol.

Diacetyloleanol was first investigated with respect to its haviour on heating. This derivative, after recrystallisation from etic anhydride, melted at 208°. Determinations of its optical tation and molecular weight gave the following results:

0·4636, made up to 20 c.c. with chloroform, gave α_D +2°52′ in a 2-dcm. tube, whence $[\alpha]_D$ +61·9°.

0·5570, in 25·13 of benzene, gave Δt −0·26°. M.W.=426.

$C_{35}H_{54}O_5$ requires M.W.=554.

The somewhat low result of this molecular-weight determination ay be accounted for by the great readiness with which diacetyl-anol undergoes partial hydrolysis.

A quantity (2 grams) of diacetyloleanol was heated in a distilla-n apparatus for some time at 240°, when a volatile substance s evolved, and collected in the receiver. This distillate was

identified by its general properties and boiling point as acetic anhydride. The solid residue in the distillation flask was dissolved in a small amount of hot petroleum (b. p. 90—120°), and boiling ethyl acetate added. A substance then separated in small, colourless, flattened prisms, which melted at 315—316°:

0·0995 * gave 0·2860 CO_2 and 0·0892 H_2O. C=78·4; H=10·0.

$C_{66}H_{102}O_7$ requires C=78·7; H=10·1 per cent.

It is thus evident that the change undergone by diacetyloleanol on heating is analogous to that suffered by diacetylprunol (Power and Moore, *loc. cit.*), and proceeds according to the following equation:

$$2C_{35}H_{54}O_5 = C_{66}H_{102}O_7 + (CH_3 \cdot CO)_2O.$$

Oxidation of Oleanol with Potassium Permanganate. Formation of Oleanone, $C_{29}H_{46}O_4$.

A quantity (10 grams) of oleanol was dissolved in glacial acetic acid, and a solution of 7 grams of potassium permanganate in a large volume of 95 per cent. acetic acid then gradually added. After keeping the mixture for an hour it was decolorised by means of sulphur dioxide, when, on pouring the solution into water, a quantity of solid was precipitated. The latter was isolated by means of ether, and the ethereal solution shaken with aqueous alkalis. This treatment, however, removed only acetic acid and relatively small amounts of amorphous products. The ethereal solution was then evaporated, and the residue crystallised from ethyl acetate. This was achieved only with considerable difficulty, owing to the great tendency of the product to separate in a colloidal condition. The material which had been once crystallised from ethyl acetate was then recrystallised several times from methyl alcohol, when it appeared to be dimorphous. It formed either glistening, colourless needles, or elongated, lustrous plates, both forms melting at 304°. The yield was about 40 per cent. of the weight of the oleanol employed:

0·1299 gave 0·3625 CO_2 and 0·1170 H_2O. C=76·1; H=10·0.

0·1331 „ 0·3712 CO_2 „ 0·1202 H_2O. C=76·0; H=10·0.

$C_{29}H_{46}O_4$ requires C=76·0; H=10·0 per cent.

It appears, therefore, that on oxidation oleanol suffers the loss of the elements C_2H_4 and the addition of one atom of oxygen. It is highly probable that the resulting product, $C_{29}H_{46}O_4$, is a ketone, although no oxime could be prepared from it, and it is proposed to designate it *oleanone*.

Oleanone is moderately soluble in most organic solvents, and i

* Dried at 130°.

determination of its optical rotatory power gave the following result:

0·3760, made up to 20 c.c. with chloroform, gave $\alpha_D + 1°31'$ in a 2-dcm. tube, whence $[\alpha]_D + 40·4°$.

Diacetyloleanone, $C_{29}H_{44}O_4(CO·CH_3)_2$.—A quantity of oleanone was heated for some time with acetic anhydride, after which the mixture was poured into water, and the resulting solid collected. The latter was crystallised from a mixture of alcohol and ethyl acetate, when pure *diacetyloleanone* was obtained. This substance, like the corresponding dihydroxy-ketone, appears to be dimorphous. It forms either well-defined, colourless needles, or flat plates. Both forms melt sharply at 293°:

0·1371 gave 0·3682 CO_2 and 0·1173 H_2O. C=73·2; H=9·5.

$C_{33}H_{50}O_6$ requires C=73·1; H=9·2 per cent.

A determination of the specific rotatory power gave the following result:

0·3966, made up to 20 c.c. with chloroform, gave $\alpha_D + 2°27'$ in a 2-dcm. tube, whence $[\alpha]_D + 61·8°$.

Unlike diacetyloleanol, this diacetyl derivative does not undergo hydrolysis with the formation of a monoacetyl derivative when heated with 75 per cent. alcohol.

Monoacetyloleanone, $C_{29}H_{45}O_4·CO·CH_3$.—A considerable quantity of impure material contained in the mother liquors from the crystallisation of crude diacetyloleanone was fractionally crystallised, when, in addition to the last-mentioned compound, a small amount of another substance was obtained. The latter formed well-defined, colourless needles, melting at 260°:

0·1038 gave 0·2831 CO_2 and 0·0878 H_2O. C=74·4; H=9·4.

$C_{31}H_{48}O_5$ requires C=74·4; H=9·6 per cent.

This substance thus appeared to be *monoacetyloleanone*, and, when hydrolysed with alcoholic potassium hydroxide, oleanone was regenerated from it. It is more soluble in alcohol and less so in ethyl acetate than the corresponding diacetyl derivative, but is freely soluble in chloroform. Its optical rotatory power was determined with the following result:

0·4147, made up to 20 c.c. with chloroform, gave $\alpha_D + 3°3'$ in a 2-dcm. tube, whence $[\alpha]_D + 73·5°$.

When the ketone was regenerated from either of its acetyl derivatives the product obtained usually consisted of a mixture of the above-mentioned dimorphous forms.

Action of Dilute Acetic Acid on Oleanone.

The oxidation of oleanol necessitated the use of a large volume of acetic acid (3 litres for 10 grams of the alcohol), and this was

also inconvenient for the isolation of the oxidation product. In a number of experiments, therefore, it was sought to recover the greater part of the acetic acid by distillation in a vacuum before the reaction mixture containing the oxidation product had been poured into water. When this was done, however, it was found very difficult, or impossible, to isolate any pure oleanone from the oxidation product, the latter being, for the most part, uncrystallisable. It was thus evident that the evaporation of the acetic acid with the aid of heat had caused some change to take place, and it was at first thought that this might be due to the partial acetylation of the oxidation product by the acetic acid in the presence of the manganous sulphate which had been formed during the treatment of the oxidation mixture with sulphur dioxide. A quantity (1 gram) of pure oleanone was therefore dissolved in acetic acid, and such an amount of manganous sulphate added, dissolved in a little water, as would have been formed during the preparation of one gram of oleanone. The mixture was boiled for three hours, after which it was concentrated in a vacuum and poured into water. The product was then extracted with ether, when some yellow, uncrystallisable material was obtained. The latter was heated for some time with acetic anhydride, after which the mixture was poured into water, and the resulting solid collected. The latter was crystallised several times from dilute alcohol, when small colourless plates were obtained, which, on heating, first softened and then melted at 324°. This substance was evidently a new compound, being quite distinct from diacetyloleanone, and it was thus evident that heating with acetic acid and manganous sulphate did not cause simply partial acetylation, as had been thought, but that some more profound change had occurred.

The action of anhydrous acetic acid alone on oleanone was therefore investigated, but, after boiling for several hours, the original ketone could be recovered unchanged. When, however, a small amount of water was added to a solution of oleanone in boiling glacial acetic acid, a pink colour rapidly developed, which gradually changed to green, and finally to a faint violet tint. On isolating the resulting product, only uncrystallisable material was obtained, but, on acetylation, the latter yielded the above-described acetyl derivative, melting at 324°. It is evident, therefore, that oleanone is radically changed by the action of hot dilute acetic acid.

The *diacetyl* derivative, $C_{30}H_{76}O_7(CO\cdot CH_3)_2$ (m. p. 324°), was moderately soluble in alcohol and ethyl acetate, but more readily so in chloroform or benzene. After drying at 125°, it yielded the following results:

0·1537 gave 0·4164 CO_2 and 0·1308 H_2O. C=73·9; H=9·4.
0·1067 „ 0·2896 CO_2 „ 0·0922 H_2O. C=74·0; H=9·6.
0·5208, in 24·0 of benzene, gave Δt –0·13°. M.W.=853.

$C_{54}H_{82}O_9$ requires C=74·1; H=9·4 per cent. M.W.=874.

A quantity of the acetyl derivative was hydrolysed by means of alcoholic potassium hydroxide, and the resulting substance isolated. The latter was crystallised from ethyl acetate containing a small amount of alcohol, when it separated in very thin, colourless plates, which melted at 312°:

0·1028 gave 0·2814 CO_2 and 0·0926 H_2O. C=74·7; H=10·0.

$C_{50}H_{78}O_7$ requires C=74·7; H=9·9 per cent.

Action of Acetic and Hydrochloric Acids on Diacetyloleanone.

A quantity (4 grams) of diacetyloleanone was dissolved in glacial acetic acid, and 15 per cent. hydrochloric acid added to the hot liquid until a faint cloudiness was produced. The mixture was then boiled for some time, when the previously-described cycle of colour changes occurred, at the completion of which a substance separated from the boiling liquid in colourless, glassy plates. After recrystallisation from methyl alcohol, this substance melted at 32?°:

0·1417 gave 0·3904 CO_2 and 0·1226 H_2O. C=75·2; H=9·6.
0·1316 „ 0·3626 CO_2 „ 0·1154 H_2O. C=75·2; H=9·7.

$C_{52}H_{80}O_8$ requires C=75·0; H=9·7 per cent.

This compound proved to be the *monoacetyl* derivative of the previously-described dihydroxy-compound, melting at 312°. On hydrolysis with alcoholic potassium hydroxide it yielded the latter, and on acetylation it gave the diacetyl derivative. (Found, C=74·1; H=9·6. Calc., C=74·1; H=9·4 per cent.) The melting point of the diacetyl derivative when prepared in this manner, however, could not be raised above 292°, but this was doubtless due to the persistent retention of a very small amount of impurity. In all other respects the two preparations were identical, and no lowering of the melting point occurred on mixing them.

Oxidation of Oleanone with Chromic Acid.

As oleanone could not be further oxidised by means of potassium permanganate, recourse was had to the use of chromic acid.

A quantity (10 grams) of oleanone was dissolved in 1 litre of glacial acetic acid, and a solution of 13 grams of chromic acid in 50 c.c. of 75 per cent. acetic acid gradually introduced, the mixture being stirred, and maintained at 55—60°. Sulphur dioxide was

then passed into the mixture to remove any excess of chromic ac
and the solution poured into water. The mixture was subsequen
extracted with ether, and the ethereal solution deprived of ac
acid by means of aqueous potassium hydroxide, washed, dried, a
concentrated. A sparingly soluble, crystalline substance t
separated from the solution. This was most conveniently recry
lised by extraction with ether in a Soxhlet apparatus, when
formed thin, lustrous, colourless plates, melting at 275°. The yi
of pure material was 4·5 grams from 10 grams of oleanone:

0·1272 gave 0·3586 CO_2 and 0·1062 H_2O. C=76·9; H=9·3.
0·1357 „ 0·3811 CO_2 „ 0·1151 H_2O. C=76·6; H=9·4.
$C_{29}H_{42}O_4$ requires C=76·7; H=9·3 per cent.

This *compound* is thus seen to be formed from oleanone by t
loss of 4 atoms of hydrogen. It was found to contain only o
hydroxyl group, and is probably a diketone.

A small quantity of the substance $C_{29}H_{42}O_4$ was acetylated b
means of acetic anhydride, and the product crystallised fr
absolute alcohol. Long, colourless, hair-like needles were t
obtained, which melted at 268°:

0·1027 gave 0·2815 CO_2 and 0·0842 H_2O. C=74·8; H=9·1.
0·3404, in 23·56 of benzene, gave Δt −0·147°. M.W.=492.
$C_{31}H_{44}O_5$ requires C=75·0; H=8·9 per cent. M.W.=

This *monoacetyl* derivative is moderately soluble in alcoh
somewhat more so in ethyl acetate, and readily so in chloroform
benzene.

Action of Potassium Hydroxide on the Compound $C_{29}H_{42}O_4$.

The substance $C_{29}H_{42}O_4$ could be recovered unchanged after bei
heated for a short time with fairly dilute alcoholic potassiu
hydroxide, and it could therefore be regenerated from its ace
derivative. When, however, stronger alkali was employed, and t
heating was more prolonged, further changes took place.

A quantity of the substance $C_{29}H_{42}O_4$ (m. p. 275°) was dissolv
in fairly concentrated alcoholic potassium hydroxide, and t
mixture heated for two hours. The liquid was then poured in
water, acidified, and extracted with ether. On evaporation of t
ether a product was obtained, which, when crystallised from
mixture of ethyl acetate and alcohol, separated in small, t
prisms, melting at 315°. The yield of the latter was by no mea
quantitative, and the mother liquors contained uncrystallisa
material:

0·1017 gave 0·2867 CO_2 and 0·0849 H_2O. C=76·9; H=9·3.
0·1406 „ 0·3970 CO_2 „ 0·1182 H_2O. C=77·0; H=9·3.
$C_{29}H_{42}O_4$ requires C=76·7; H=9·3 per cent.

This *substance* therefore appears to be isomeric with the compound $C_{29}H_{42}O_4$ (m. p. 275°), from which it was obtained. A mixture of the two isomerides melted at 250—256°.

The new isomeride, melting at 315°, yielded a *monoacetyl* derivative on treatment with acetic anhydride. This derivative crystallised from ethyl acetate in colourless needles, melting at 308°:

0·1106 gave 0·3046 CO_2 and 0·0920 H_2O. C = 75·1; H = 9·2.
$C_{31}H_{44}O_5$ requires C = 75·0; H = 8·9 per cent.

Another portion of the original compound, $C_{29}H_{42}O_4$ (m. p. 275°), was dissolved in concentrated alcoholic potassium hydroxide, and the mixture boiled for three days, after which it was evaporated almost to dryness. The residue was then poured into water, acidified, and extracted with ether. On evaporating the ether a product was obtained, from which neither of the isomeric substances, $C_{29}H_{42}O_4$, could be obtained, and which was, for the most part, uncrystallisable. It yielded, however, a small amount of a substance, which crystallised in small leaflets, melting at 87—88°, and had the characters of a higher fatty acid:

0·0578 gave 0·1652 CO_2 and 0·0682 H_2O. C = 78·0; H = 13·1.
$C_{23}H_{46}O_2$ requires C = 78·0; H = 13·0 per cent.

The formation of a fatty acid, $C_{23}H_{46}O_2$, from the substance $C_{29}H_{42}O_4$ would account for the major portion of the molecule of oleanol, and would greatly facilitate the elucidation of the constitution of the latter. The change might take place according to the following equation:

$$C_{29}H_{42}O_4 + 4H_2O = C_{23}H_{46}O_2 + C_6H_4O_6.$$

Unfortunately, however, this point cannot be considered as definitely established, since the amount of material available only permitted of one further small experiment being conducted, and the latter did not result in the isolation of any more of the fatty acid in question. It is difficult to see, however, how the acid $C_{23}H_{46}O_2$ (m. p. 87—88°) could have been introduced from an extraneous source, particularly as no compound possessing this composition and melting point has hitherto been known. An acid possessing the same formula, but melting at 68°, has been shown to occur in olive leaves (Power and Tutin, *loc. cit.*), but it is impossible for any of this to have been occluded in the compound $C_{29}H_{42}O_4$ (m. p. 275°), which was hydrolysed, since the latter was prepared from pure oleanol, melting at 304°.

The action of concentrated alcoholic potassium hydroxide on oleanol itself was investigated, but was found to bring about no change.

Oxidation of Oleanol with Chromic Acid.

Oleanol was oxidised with chromic acid under the same conditions as those described in connexion with the oxidation of oleanon. At the completion of the oxidation the acetic acid solution was poured into water and extracted repeatedly with ether. The ethereal solution was then shaken with aqueous alkali, which removed acetic acid and a considerable amount of a mixture of solid carboxylic acids. The ethereal liquid then contained the above-described substance, $C_{29}H_{42}O_4$ (m. p. 275°), the yield of which was about 10 per cent. of the weight of the oleanol employed.

The above-mentioned mixture of carboxylic acids could not be crystallised, nor could any crystalline ester or salt be obtained from it. It was therefore converted into the barium salt, and the latter precipitated in seven fractions by concentrating its aqueous solution. The acid was then recovered from each of the fractions of barium salt, and the resulting products, all of which were amorphous, dried at 125°. Their analysis and the determination of their neutralisation values gave the following results:

Fraction.	Percentage of carbon.	Percentage of hydrogen.	Neutralisation value.
1	69·0	8·4	236
2	68·6	8·3	237
3	71·7	8·6	268
4	70·7	8·6	268
5	69·4	8·5	243
6	69·7	8·4	230
7	68·3	8·0	221

It is thus evident that the direct oxidation of oleanol by means of chromic acid results in the formation of at least three carboxylic acids, in addition to the above-described substance, $C_{29}H_{42}O_4$.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

CCXVIII.—*The Interaction of Sodium Amalgam and Water.*

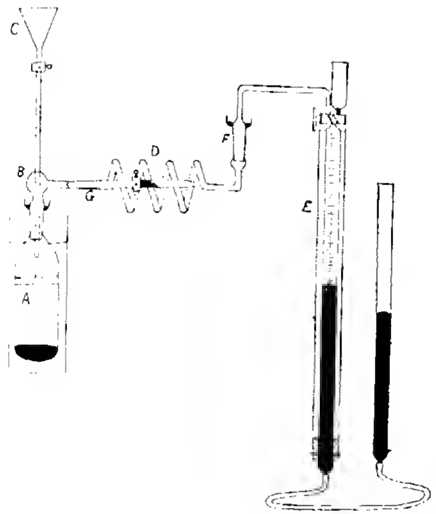
By HERBERT BRERETON BAKER and LESLIE HENRY PARKER.

THE fact that water prepared under special conditions acted with a strikingly slower velocity on sodium amalgam than did ordinary distilled water was observed by one of us two years ago (Baker, *Trans. Faraday Soc.*, 1910–11, **6**, 119). The original qualitative experiment was performed in the following manner.

Water was distilled from a copper or Jena-glass boiler, and the

steam passed through a carefully cleaned copper tube, made without brazing, which acted as a condenser. Two or three inches of the copper tube were heated to redness by a Bunsen burner before the steam was condensed. The tube was suitably bent to prevent any spray from the boiler being collected in the receiver. For the purpose of the experiments, after about one-sixth of the quantity of water taken had been distilled over, the distillate was collected, the distillation being stopped when a similar quantity was left in the boiler. Two Jena-glass test-tubes were then cleaned with a mixture of nitric and chromic acids, rinsed, and steamed for half-

FIG. 1.



an-hour. One was half-filled with this special water, and the other with ordinary distilled water. Into each a few c.c. of sodium amalgam were filtered through a dried filter paper, pierced with small holes.

Whilst the action in the tube containing ordinary distilled water spread very quickly over the surface of the amalgam, and hydrogen was evolved at a rapid rate, in the case of the specially distilled water the action was confined practically to one small point on the surface of the amalgam, and the hydrogen was evolved as a fine stream, at an obviously slower rate than in the case of the ordinary distilled water. An apparatus (Fig. 1) was then constructed to measure accurately the volume of gas evolved.

A is the reaction-vessel, which consisted of a large, thick Jena-glass test-tube, with its neck drawn out, into which was ground the open stopper *B*, of soft glass.

Through *B* was sealed the tap-funnel *C*, the upper portion of which was made conical to accommodate a filter paper. Into *B* was also sealed the worm *D*, to give flexibility to the apparatus. Between *B* and *D* a side-tap *G* was inserted, to allow an independent opening to the atmosphere when necessary. The whole was then put in connexion with the nitrometer *E*, by means of the ground joint *F*. The two ground joints and the tap *G* were protested by mercury seals. The mode of carrying out the experiment was to put a quantity of the water into *A*, fit the apparatus together, and filter in the amalgam through *C*. The reaction-vessel was graduated for 50 c.c. and 55 c.c., and except where otherwise stated, 50 c.c. of water and 5 c.c. of amalgam were taken for the test.

Before each experiment, the whole apparatus was cleaned as described for the test-tubes in the qualitative experiment.

The reaction-vessel and the nitrometer were surrounded with water jackets to keep them at as constant a temperature as possible. All the experiments were conducted at the ordinary temperature, and leaks were proved absent by leaving the apparatus together, empty, overnight, under diminished pressure.

As a comparison, below is a table showing the rates of evolution of hydrogen, firstly, from a specimen of ordinary distilled water, secondly from a specimen of the specially distilled water.

Time in hours.	Ordinary distilled water.	Specially distilled water.
1	23·7 c.c. H_2	1·4 c.c. H_2
2	—	2·6
3	54·0	—
4	—	—
5	—	4·0
6	77·0	—
7	—	4·6

The temperature of reaction in each case was 10°.

Between the times at which the readings were taken, the pressure in the apparatus was kept at about 20 mm. under atmospheric pressure. The results obtained seemed of sufficient interest to justify more detailed investigation.

The special water was prepared in quantity by distillation from a copper boiler made without brazing, with a copper condenser screwed into the top. The water was stored in a Jena-glass bottle fitted with a siphon tap, and protected by a soda-lime tube. The water could be stored in this way for a week or more without much alteration of its activity.

The sodium amalgam for use in these experiments was prepared

with redistilled mercury, and it contained rather less than 1 per cent. of sodium.

As a check on the reaction, after the reaction had been going on for some time, the apparatus was quickly disconnected, and 25 c.c. of the solution drawn out at once, and titrated with standard hydrochloric acid solution.

It was noted at first that the alkalinity of the solution always corresponded with a volume of hydrogen in excess of that actually measured.

Experiment.	Time in hours.	c.c. H_2 observed.	c.c. H_2 calculated from titration.
A	19	52·5	70·2
B	20½	21·8	25·8
C	6	30·1	33·9

No leak could be detected in the apparatus by further testing, and also during the course of the reaction the pressure was kept below that of the atmosphere, so that any leak would have been a leak *inwards*.

It was then thought that the excess volume of gas indicated by the titration might be due to the original alkalinity of the amalgam itself.

To test this, a few c.c. of the amalgam were shaken for a few seconds with about 10 c.c. of the special water in a tap-funnel. No visible action took place in this short time, so that the water gained no alkalinity from direct action on the amalgam. The water was separated off and titrated, and in spite of the small quantity of amalgam taken, showed an alkalinity corresponding with 0·6 c.c. of hydrogen.

It was then thought advisable to filter the amalgam as efficiently as possible, and specially cleaned asbestos was chosen as the filtering agent.

Asbestos wool was allowed to soak for twenty-four hours in a mixture of concentrated hydrochloric and nitric acids. It was then thoroughly washed with distilled water until the latter showed no acid reaction, and then heated in a muffle furnace for several hours.

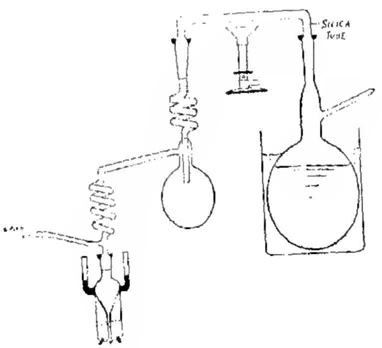
The tap-funnel *C* in the apparatus described above was then replaced by a glass tube of about 8 mm. diameter, lightly packed with the asbestos, the latter held in place at a constriction at the lower end by a roll of filter paper. To the upper end of this filtering column was sealed a wider portion, fitted with a ground stopper. The amalgam was filtered in through a punctured filter paper, and the stopper quickly inserted. This form of the apparatus also had the advantage of abolishing the unprotected tap in the tap-funnel.

The effect of this was to diminish the discrepancy between the observed volume of gas and that calculated from the titration although not to eliminate it entirely.

Experiment.	Time in hours.	c.c. H_2 observed.	c.c. H_2 calculated from titration.
A	4	2·9	4·5
B	6	27·6	34·7
C	6	4·0	4·7
D	4	10·8	11·8
E	2	5·3	5·3
F	6	6·0	6·0

The next point thought to be of importance to the investigation was to determine whether the rate of action of the water on the amalgam was any sort of function of the conductivity.

FIG. 2.



For this purpose different specimens of water were obtained from various sources.

The conductivities were measured in a specially made cell of Jena-glass having a capacity of about 75 c.c., containing platinum plates about 1 cm. × 2 cm. and 1 mm. apart.

The cell was supplied with a tube ground into the neck, so that it could be sealed off if necessary when distilling in a vacuum. It was not found possible to obtain water of much less than 1 gemmho conductivity, as a general rule; this was possibly due to the London atmosphere. Even by distilling in a vacuum, water of much less conductivity than this was not obtained. It was thought that light might be thrown on the cause of the inactivity of the water by testing water which had been subjected to different methods of treatment.

Except where otherwise stated, ordinary distilled water was placed the boiler.

Specimens of water were obtained as follows:

(1) From the copper boiler and condenser as described above. This gave water varying in conductivity from 0·7 gemmho to ·5 gemmhos.

(2) Water kindly supplied by Mr. Bousfield from his special ill. This on reaching us had a conductivity of about 1·8 gemmho.

(3) From a specially modified Bousfield still (Fig. 2), made roughout of Jena-glass, except that a silica tube was fitted into e apparatus by mercury-protected ground joints, in passing rough which the steam was heated to redness.

In collecting the water for conductivity determinations, the cell as surrounded by ice, and the distillation carried out in a vacuum st above the ordinary temperature. A little potassium hydrogen lphate was placed in the boiler. This gave water of about 1·7 to) gemmhos conductivity.

(4) A large platinum still was used of a capacity of about 1 litre, d the various parts could be screwed together without the use of y extraneous material.

A current of air freed from carbon dioxide was passed in through e still-head. The condensed steam was received either in a atinum bottle or in the reaction vessed itself, which was protected a soda-lime tube, so that the water was distilled and collected an atmosphere free from carbon dioxide. This gavo water rying in conductivity from 1 to 2 gemmhos. Superheating the am at the still-head, either by a Bunsen burner or by means an electric furnace surrounding it, did not alter the conducity to any appreciable extent.

The following table, arranged in order of increasing conductivity, ws that there is no regular relation between the activity of a

Source of water.	Conductivity $\times 10^{-6}$.	Activity in c.c. H_2 per hour.
Platinum still	1·08	2·9
Modified Bousfield still	1·3	1·7
Copper still	1·38	10·8
Copper still	1·38	1·4
Platinum still	1·48	1·9
Modified Bousfield still	1·76	1·5
Mr. Bousfield	1·86	3·2
Platinum still	1·86	0·63
Modified Bousfield still	1·9	1·3
Platinum still	2·08	1·0
Platinum still	2·17	2·4
Copper still	2·31	1·4
Platinum still	3·6	5·1
Copper still	3·8	1·0
—	4·4	2·8
Copper still	12·9	1·2

specimen of water on the amalgam and its conductivity, althoug as a general rule, the purer waters were less active.

Some of the specimens of water had been submitted to spec treatment, such as exposure to metals, radium bromide, etc., th individual effects of which it is hoped to describe in a furth communication.

That one of the main factors in the decrease of activity was th superheating of the steam is shown by the following tables:

Time in hours.	1.	2.	3.	4.	5.
c.c. H_2 from distilled water redistilled, steam *not* superheated.	1·2	3·3	5·2	7·0	9·3
	0·46	2·2	4·0	5·5	7·9
	3·24	7·7	9·9	12·5	14·3
	2·3	5·1	8·7	11·0	12·0
c.c. H_2 from distilled water redistilled, steam superheated.	0·5	1·3	1·8	2·9	—
	1·0	1·7	2·5	3·0	3·9
	0·46	1·3	2·6	3·0	4·3
	0·28	1·1	2·03	2·9	3·3
	unmeasurable	0·6	1·3	—	2·1

The reason for this decrease in activity was still obscure. Th supposition that the inactive water might be (H_2O) molecul associated to a greater extent than in the case of ordinary act water, was rather discounted by the fact that the boiling a freezing points of this water were not sensibly different from th of ordinary distilled water.

The effect of the reduction of pressure on the reaction was th tried, the reaction-apparatus being exhausted through the tap and the readings taken at constant volume at a fixed point on t nitrometer. Knowing the internal volume of the apparatus to t point, and measuring the difference in level of the mercury in bo limbs of the nitrometer, the volume of gas given off over a defin period could be calculated.

	Experiments under diminished pressure.				Comparative experiments, ordinary pressure throughout.	
Experiment.	Time in hours.	Average pressure. mm.	c.c. H_2.	Difference per hour in c.c. H_2	c.c. H_2.	Difference per hour in c.c. H_2
A.	1	132	7·3	7·3	2·2	2·2
	2	260	13·5	6·2	9·4	7·2
	3	348	16·6	3·1	14·6	5·2
	4	397	18·7	2·1	17·8	3·2
	5	430	20·1	1·4	19·7	1·9
	6	454	21·3	1·2	21·2	1·5
B.	1	138	8·1	8·1	unmeasurable	unmeasurabl
	1½	259	13·1	5·0	0·9	0·9
	3	381	21·4	8·3	2·6	1·7
	4	510	26·7	5·3	3·4	0·8
	5	587	29·8	3·1	4·2	0·8
	6	630	31·9	2·1	4·9	0·7

...riments under diminished pressure.					Comparative experiments, ordinary pressure throughout.	
...eri-ment.	Time in hours.	Average pressure. mm.	c.c. H_2.	Difference per hour in c.c. H_2.	c.c. H_2.	Difference per hour in c.c. H_2.
C.	1	121	7·6	7·6	0·3	0·3
	2	258	14·7	7·1	1·8	1·5
	3	386	21·4	6·7	2·8	1·0
	4	488	25·8	4·4	3·2	0·4
	5	570	29·0	3·2	3·7	0·5
	6	612	31·5	2·5	4·1	0·4
D.	1	242	20·1	20·1	0·8	0·8
	2	445	21·9	1·8	2·3	1·5
	3½	471	22·8	0·9	3·1	0·8
	4½	484	23·2	0·4	3·8	0·7
	5½	491	23·6	0·4	4·1	0·3
	6½	498	23·9	0·3	4·6	0·5

It will be seen from this table that whilst the action proceeded ...h moderate regularity while under constant pressure, in the ...se of the experiments under diminished pressure the rate ...creased as the pressure in the apparatus increased, until as the ...essure more nearly approached that of the atmosphere, so the ...te of action became more and more comparable with that of the ...mparative experiment carried out under the ordinary pressure.

In this connexion, another important point that was noticed was ...e fact that whenever the reaction was progressing quickly, for ...stance, under low pressure, the action was taking place all over ...e surface of the amalgam; but the slower the rate, the more ...ited became the area of activity, until with the least active ...ecimens of water, under the best conditions, the action was ...fined to a small point about the centre of the surface of the ...algam.

A possible explanation of these facts was the supposition that a ...m of hydrogen was formed over the surface of the amalgam, ...ich protected it more or less from the action of the water; and ...at, in the case of the less pure waters, by some means or other ...is film was removed or ruptured. Also the explanation of the ...alised action might be found in assuming some small impurity ...the amalgam at that point, which was less electropositive than ...e sodium, and formed an electric couple with it. If this were ... and if the conditions were made to approximate to those in a ...taic cell, the rate of evolution of hydrogen should become some ...t of function of the conductivity of the water or solution.

Further experiments were therefore made, at constant pressure, ...th a piece of platinum wire in the reaction-vessel which was ...vered partly by the amalgam and partly by the water.

The results are given in the following table:

Experiment.	Time in hours.	c.c. H_2. Water alone.	Difference in c.c. H_2 per hour.	c.c. H_2 Water + Pt wire.	Difference c.c. H_2 per hour.
A	1	1·6	1·6	1·6	1·6
	2	3·4	1·8	4·2	2·6
	3	4·5	1·1	7·3	3·1
	4	5·8	1·3	11·0	3·7
	5	7·5	1·7	16·0	5·0
	6	8·7	1·2	22·2	6·2
	7	10·5	1·8	31·0	8·8
B	1	0·6	0·6	0·9	0·9
	2	1·5	0·9	2·5	1·6
	3	2·3	0·8	4·3	1·8
	4	3·2	0·9	6·6	2·3
	5	4·0	0·8	9·8	3·2
	6	4·8	0·8	13·8	4·0

From this table it will again be observed that the action between the amalgam and water alone proceeds fairly regularly, but although in the case where the platinum wire is inserted the action proceeds quicker and quicker as time goes on, this acceleration is nothing like so great as the increase which must take place in the conductivity of the solution as the sodium hydroxide accumulates.

In order further to investigate this, the rate of the reaction at the *commencement* was studied by adding various quantities of a dilute solution of pure sodium hydroxide to samples of the water before the amalgam was put in. The conductivities of the solutions were measured.

The sodium hydroxide was prepared by allowing small pieces of sodium to deliquesce on a porcelain funnel under a bell-jar inverted over water, replacing the ordinary air by air freed from carbon dioxide.

Conductivity $\times 10^{-6}$...	0·73	0·78	3·45	8·64	9·15	29·8	46·5	117·4
Time in hours.	c.c. H_2.	c.c. H_2.	c.c. H_2.	c.c. H_2.	c.c. H_2.	c.c. H_2.	c.c. H_2.	c.c. H_2.
1	2·0	0·4	1·6	1·3	1·8	1·4	0·2	[illegible]
2	5·0	2·2	4·2	3·6	4·5	3·1	2·6	[illegible]
3	9·2	4·3	8·4	6·3	7·1	5·7	5·7	5·5

It will be seen from this that the addition of sodium hydroxide does not alter in any regular way the rate of commencement of the reaction.

The explanation propounded above, therefore, does not seem to be tenable.

A purer form of amalgam was also prepared by distilling sodium into redistilled mercury in a vacuum. As will be seen from the following table, the reaction was slow, but not of an order differing remarkably from previous reactions.

Time in hours	1.	2.	3.	4.	5.	6.
c.c. H_2	0·3	1·2	2·0	2·8	3·8	5·0

It appears, therefore, that there is no connexion between the nductivity of the water and the activity of its reaction with dium amalgam. This being so, the activity of ordinary water ust be due to the presence of some impurity which is not elimin- ed by the ordinary processes employed for the purification of ter, and which does not when present in water appreciably affect electrical conductivity. The only impurity satisfying these nditions would seem to be hydrogen peroxide.

To test this, comparison was made of the activity of our purified ter (1) alone, and (2) with the same water to 50 c.c. of which d been added 1 drop of a 1 per cent. solution of distilled hydrogen roxide.

Time in hours.	c.c. H_2 from water alone.	c.c. H_2 from water with H_2O_2.
½	unmeasurable	0·6
1	,,	3·8
1½	1·3	10·2
2	2·2	17·6
3	4·1	32·4

Even at this state of dilution (about 1 in 100,000) the hydrogen roxide therefore has increased the activity enormously.

The conductivity of the water was not appreciably altered by is small quantity of hydrogen peroxide.

Although the amount of hydrogen peroxide added was sufficient give a very strong colour with titanium oxysulphate before the action was started, the solution at the end of the experiment did t show a trace of colour with this reagent.

Apparently the hydrogen peroxide possessed potential powers starting the reaction, but was then reduced by the nascent drogen.

It was then thought possible that the differing activities of fferent samples of water might be due to the presence of varying antities of hydrogen peroxide. Hydrogen peroxide, being latile in steam, would pass over in an ordinary distillation, but ould be decomposed if the vapour were heated to redness. Tap- ater, the most active of the specimens tried, was found to give no sible colour with titanium oxysulphate; but when potassium dide and starch, with a trace of ferrous sulphate, were used, a rong blue colour developed. Not even this very delicate test owed any colour, however, either with water distilled from a pper vessel or the special water.

Fifty c.c. of water were then synthesised by passing pure ydrogen and oxygen, obtained from the electrolysis of baryta ater, over palladium.

This water was found to act rapidly on sodium amalgam:

Time in hours	1.	2.	3.
c.c. H_2	6·5	17·4	24·7

Traube has shown (*Ber.*, 1893, **26**, 1471) that palladium-hydrogen, in the presence of oxygen and water, yields hydrogen peroxide. The next point to be proved was whether the test given above in tap-water was due to hydrogen peroxide or to some other oxidising agent.

Tap-water was distilled from a Jena-glass boiler, to which was sealed a Jena-glass condenser.

The middle fraction gave no colour by the potassium iodide and ferrous sulphate test, but the residue in the boiler gave a strong reaction. On distilling tap-water, however, under the same conditions, but having in addition a few pieces of platinum wire or a little finely-divided pure silver in the boiler, neither the distillate nor the residue gave the test, the hydrogen peroxide, if present, having been decomposed by these metals. It was then thought to be of interest to compare the respective activities of these various samples, in relation to their possible content of hydrogen peroxide.

Time in hours.	*A.* c.c. H_2.	*B.* c.c. H_2.	*C.* c.c. H_2.	*D.* c.c. H_2	*E.* c.c. H_2.
1	18·5	4·7	5·8	4·6	8·7
2	28·9	9·6	13·3	11·5	15·2
3	34·8	14·8	19·8	17·4	22·6
4	—	21·8	26·9	23·4	30·8

(*A*) Tap-water. Gave a strong colour with potassium iodide, ferrous sulphate, and starch.

(*B*) Tap-water distilled from Jena-glass apparatus, with pieces of platinum wire in the boiler. Neither the distillate nor the residue gave the above test.

(*C*) Repetition of (*B*), using silver instead of platinum. Neither the distillate nor the residue gave the test.

(*D*) Tap-water alone distilled from Jena-glass vessel. The distillate did not give the test, but the residue in the boiler did.

(*E*) Residue from (*D*) distilled almost to dryness. The distillate now gave the test, but not so strong as for tap-water.

The explanation for the activity of water on sodium amalgam seems therefore to be found in the presence of traces of hydrogen peroxide.

Addition of hydrogen peroxide has been shown above to increase the activity enormously, and where the colour tests have shown the presence of hydrogen peroxide, that specimen of water has been shown to be more active than where the test has not been delicate enough to detect it.

All the very inactive specimens of water have been prepared under conditions which would favour the decomposition of hydrogen peroxide; for example, the superheating of the steam in the copper condenser, and the distillation from a platinum

paratus, again superheating the steam. One distillation by means the latter method gave the most striking result yet attained, own in the following table:

me in hours ...	1.	2.	3.	4.	5.	6.
. H	unmeasurable	unmeasurable	unmeasurable	0·1	0·4	0·5

The explanation propounded above would also account for the ct that the activity of the water is no function of its conducivity, it having been shown above that the addition of a small antity of hydrogen peroxide to a sample of water, whilst increasg its activity very much, did not appreciably alter its conducity.

On this explanation, specimens *B*, *C*, and *D* above, whilst not ntaining enough hydrogen peroxide to give the colour reaction, t contained enough to give a considerable, and about an equal, locity to their reaction on sodium amalgam.

THE IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON, S.W.

CXIX.—*The Action of Variously Treated Waters on Sodium Amalgam.*

By LESLIE HENRY PARKER.

ITH reference to the preceding paper by Baker and Parker . 2060) on the interaction of sodium amalgam and water, the thor has investigated the effect on the activity of water subjected various treatment. Different metals were sealed up in Jena-glass sks with about 200 c.c. of the inactive water for periods varying om ten to thirty days, and their effect on the activity of the water as noted. The metals were as pure specimens as possible, and ere cleaned with dilute nitric acid, washed about twenty to twentye times with distilled water, and steamed in the flasks into which ey were to be introduced whilst the former were being cleaned.

In each case a specimen of the water alone was laid aside under milar conditions to act as a comparison.

Time in in hours.	Water alone, sealed *cold* in flask, 22 days.	Water sealed *cold* with electrolytic Cu, 12 days.	Water sealed *cold* with pure Ag, 22 days.	Water sealed *cold* with Pt, 17 days.
1	0·2 c.c. H_2	1·7	0·9	3·2
2	0·7	3·1	1·7	5·7
3	1·3	3·5	2·8	6·8
4	1·8	4·0	3·7	7·8
5	2·5	4·2	4·7	8·8
6	3·0	—	5·6	9·4

In the case of the water exposed to copper, the metal was tarnished on the surface, especially where resting against the vessel. The water gave an appreciable colour test for copper on passing hydrogen sulphide.

Time in in hours.	Water alone, sealed *boiling*, 28 days.	Water sealed *boiling* with Cu, 22 days.	Water sealed *boiling* with Hg, 19 days.	Water sealed *boiling* with Al, 20 days.	Water sealed *boiling* with Al + Ag, 17 days.
1	unmeasurable	1·1	0·7	2·3	3·0
2	0·3 c.c. H_2	1·7	1·8	4·4	6·2
3	0·5	2·6	3·3	6·0	8·8
4	1·2	3·4	4·7	8·5	11·8
5	1·5	4·3	—	11·5	13·7
6	2·2	5·5	8·0	15·4	16·3

Time in hours.	Water alone, sealed *boiling*, 21 days.	Water sealed *boiling* with Cu, 25 days.	Water sealed *boiling* with heated Ag, 24 days.
1	unmeasurable	0·9	2·8
2	0·5 c.c. H_2	2·8	7·5
3	1·3	4·9	12·3
4	2·3	7·1	18·1
5	3·6	9·7	—
6	5·0	12·4	—

Time in in hours.	Water alone, sealed *boiling*, 28 days.	Water sealed *boiling* with Cu, 27 days.	Water sealed *boiling* with Hg, 19 days.	Water sealed *boiling* with Al, 29 days.
1	unmeasurable	unmeasurable	0·5	2·3
2	0·9 c.c. H_2	1·4	2·3	6·7
3	2·1	2·7	—	11·4
4	3·6	4·0	5·5	16·5
5	5·2	5·2	7·3	21·7
6	7·2	6·1	—	—

Time in hours.	Water sealed *boiling*, 34 days.	Water sealed *boiling* with Cu, 33 days.	Water sealed *boiling* with Al, 36 days.
1	1·7 c.c. H_2	1·4	5·1
2	3·9	3·2	12·7
3	5·5	4·4	21·9
4	7·2	6·1	—
5	8·5	7·4	—

From these figures the general impression is that exposure to metals increases to some extent the activity of the water, more especially in the case of aluminium, whilst copper and mercury have not so much effect.

The explanation of this might be found in assuming the formation of a small amount of hydrogen peroxide during the long standing of the metals with the water and the oxygen dissolved in it.

If this is the case, however, hydrogen peroxide is not formed in sufficient quantity to give the test with potassium iodide, starch, and ferrous sulphate. With the more easily oxidisable metal

aluminium one would expect more hydrogen peroxide to be formed than with copper or mercury. This view is in harmony with the fact which Traube discovered (*Ber.*, 1882, **15**, 670), that considerable quantities of hydrogen peroxide were produced when zinc acted upon water in presence of oxygen, whilst he did not detect it when copper was treated in a similar manner.

However, it has been shown in the preceding paper that a trace of hydrogen peroxide is sufficient to increase the activity enormously, and thus it is quite reasonable to suppose that the quantity of hydrogen peroxide necessary to produce a small increase in the activity would be quite undetectable by the ordinary colour tests.

Further specimens of water were exposed to radium bromide for various periods. The results were certainly interesting.

Time in hours........	1.	2.	3.	4.	5.	6.
Water alone, sealed *cold*, 22 days	0·2 c.c. H_2	0·7	1·3	1·8	2·5	—
Same exposed to $RaBr_2$ (closed tube), 28 days...	1·2	2·7	4·3	6·3	8·7	11·0
Water sealed *boiling*, 28 days	unmeasurable	0·4	0·5	1·2	1·5	—
Same exposed to $RaBr_2$ (open tube), 29 days...	2·4	7·2	12·7	18·6	25·0	28·0
Water sealed *boiling*, 50 days	0·2	1·1	2·4	3·5	4·6	6·0
Same exposed to $RaBr_2$, 50 days	2·9	8·3	14·0	20·0	25·5	—
Water sealed *cold*, 27 days......................	3·2	6·1	9·2	12·0	15·2	—
Same exposed to $RaBr_2$ (closed tube), 35 days...	17·6	38·1	—	—	—	—

Exposure to radium bromide in every case has increased the activity considerably.

In support of the explanation of the varying activities of different samples of water advanced in the previous paper, namely, that hydrogen peroxide is the agent which influences the rate of interaction of sodium amalgam and water, Kailan (*Monatsh.*, 1912, **33**, 1329) has shown that water exposed to the penetrating radiations from radium bromide, in acid, neutral, or alkaline solutions, is partly transformed into hydrogen peroxide.

This would account for the increase of activity of the water so exposed, and the explanation put forward above would seem to be the only one consistent with all the observed facts.

THE IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON, S.W.

CCXX.—*Studies in the Diphenyl Series. Part V. Derivatives and Substitution Products of the Two Isomeric* o-*Dinitrobenzidines and Synthesis of Derivatives of Benzerythrene.*

By John Cannell Cain, Albert Coulthard, and Frances Mary Gore Micklethwait.

In Part II of this series (T., 1912, **101**, 2298) proof was adduced of the existence of two different *o*-dinitrobenzidines, and it was also shown that these yield two different acetyl derivatives, and, by elimination of the amino-groups, two different dinitrodiphenyls.

In order further to study the difference between these bases, several derivatives have been prepared from each (*diformyl*, *dibenzoyl*, and *disuccinyl*), each pair proving to be different.

In addition, a study of the action of phthalic anhydride and of its di- and tetra-chloro-derivatives on the two dinitrobenzidines led to results which may help to throw light on the constitution of these bases. It has been shown by Koller (*Ber.*, 1904, **37**, 2880) that when benzidine and phthalic anhydride are boiled together in aqueous suspension, the cyclic compound, phthalylbenzidine, $C_6H_4<\begin{matrix}CO\cdot NH\cdot C_6H_4\\ CO\cdot NH\cdot C_6H_4\end{matrix}$, is formed, and the unimolecular character of such compounds has been proved by Kaufler (*Annalen*, 1907, **351**, 151; *Ber.*, 1907, **40**, 3250). When, however, the above materials are heated together, 4 : 4′-diphthaliminodiphenyl,

$$C_6H_4<\begin{matrix}CO\\ CO\end{matrix}>N\cdot C_{12}H_8\cdot N<\begin{matrix}CO\\ CO\end{matrix}>C_6H_4,$$

is formed (Bandrowski, *Ber.*, 1884, **17**, 1181). On applying these two reactions to the two dinitrobenzidines, the 3 : 3′-isomeride furnished, in both cases, the cyclic compound, 3 : 3′-*dinitrophthalylbenzidine*, $C_6H_4<\begin{matrix}CO\cdot NH\cdot C_6H_3\cdot NO_2\\ CO\cdot NH\cdot C_6H_3\cdot NO_2\end{matrix}$, whilst the 3 : 5′-isomeride did not react at all in aqueous suspension, and, when heated with phthalic anhydride, gave 4 : 4′-*diphthalimino*-3 : 5′-*dinitrodiphenyl*,

$$C_6H_4<\begin{matrix}CO\\ CO\end{matrix}>N\cdot C_{12}H_6(NO_2)_2\cdot N<\begin{matrix}CO\\ CO\end{matrix}>C_6H_4.$$

It would thus appear that under these conditions 3 : 3′-dinitrobenzidine exhibits much more tendency to form a cyclic compound with phthalic anhydride than does the 3 : 5′-isomeride, and it may be that, when further results have been accumulated, Kaufler's stereochemical formula for benzidine (*Annalen*, *loc. cit.*) will be

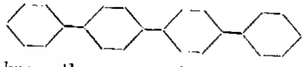
of help in deciding the influence of the nitro-groups in these reactions.

With 3 : 6-dichlorophthalic anhydride both bases gave the corresponding dichlorophthalimino-derivative, whilst with 3 : 4 : 5 : 6-tetrachlorophthalic anhydride the cyclic phthalyl compounds were produced.

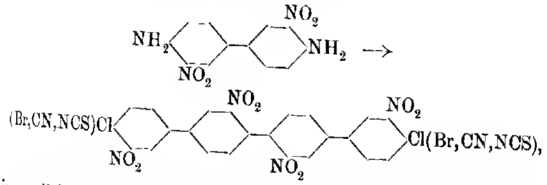
Besides the above compounds, certain bisazo-derivatives of each base have been prepared by the aid of phenol, β-naphthol, 1-naphthylamine-4-sulphonic acid (naphthionic acid) and 8-amino-1-naphthol-3 : 6-disulphonic acid (H-acid), the corresponding pairs of bisazo-compounds being found to be markedly different in each case.

Further, each base has been submitted to the diazo-reaction with the object of replacing the amino-groups by chlorine, bromine, iodine, hydroxyl, cyanogen, and the thiocyano-group.

Through this reaction the two o-dinitrobenzidines have been found to exhibit a still greater difference in their chemical behaviour than was disclosed by the reactions studied in the former paper (*loc. cit.*). In carrying out the replacement of the amino-groups by chlorine, bromine, and cyanogen, by means of copper bronze (Ullmann's method), and by the thiocyano-group (without the use of copper), 3 : 3′-dinitrobenzidine gave the expected substitution products (except in the case of bromine, see p. 2081), but 3 : 5′-dinitrobenzidine showed an entirely different behaviour. Instead of the expected substitution products, it was found that two diphenyl nuclei coalesced, with the production of derivatives of benzerythrene:

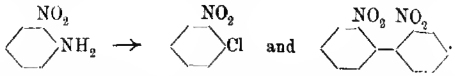


So far as we know, the compounds described in this paper are the first substitution products of this hydrocarbon that have been obtained, and their formation, represented thus:



is paralleled in an interesting manner in the case of *o*-nitroaniline, which, under similar conditions (using either copper powder or cuprous chloride), yields a mixture of *o*-chloronitrobenzene and

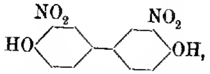
2 : 2′-dinitrodiphenyl (Niementowski, *Ber.*, 1901, **36**, 3325; Ullmann and Forgan, *ibid.*, 3803), thus:



In the replacement of the amino-group by iodine (where no copper was used), the reaction followed the normal course, the two di-iododinitro-derivatives differing from each other.

Some ten years ago, during an investigation of the action of water on dianisidine and 3 : 3′-dichlorobenzidine, bases containing acidic groups in the ortho-position with respect to the amino-groups (Cain, T., 1903, **83**, 688), it was found that the chief product in each case was a dark-coloured insoluble substance, to which a quinonoid constitution was assigned, and that only in the case of 3 : 3′-dichlorobenzidine was it possible to isolate a trace of 3 : 3′-dichloro-*p*-diphenol. It was to be anticipated, therefore, that on applying this reaction to the case of the *o*-dinitrobenzidines containing strongly acidic groups in the ortho-position to the amino-groups, difficulties might be experienced in substituting the amino-groups by hydroxyl. By carrying out the reaction in the ordinary manner, namely, by heating the bisdiazonium salts of the two dinitrobenzidines with water or dilute sulphuric acid, only traces of phenolic substances were formed, but by a variation of this method three different substances, all of the composition of the corresponding dinitrodiphenol, were obtained from 3 : 3′-dinitrobenzidine, and one dinitrodiphenol, apparently different from any of the above, was produced from 3 : 5′-dinitrobenzidine. All these dinitrodiphenols appear to be of high molecular weight, as they are brown and amorphous, and do not resemble in any way the dinitrodiphenol obtained by nitrating 4 : 4′-diphenol (see below). Since the work on dianisidine and 3 : 3′-dichlorobenzidine was carried out, it was shown by Orton, Coates, and Burdett (T., 1907, **91**, 35) that in many cases (in the benzene series) where this reaction was difficult or impossible to bring about, the substitution could be effected easily by means of sunlight. Accordingly, solutions of the diazotised bases were exposed to sunlight until no more diazonium salt was present. Incidentally this experiment showed the great stability of the diazonium salts; that from 3 : 3′-dinitrobenzidine, exposed to light in June, 1913, at the ordinary temperature (about 20°) required two weeks, and that from 3 : 5′-dinitrobenzidine, about three weeks, before the decomposition was at an end. The experiments were successful in so far as hydroxy-compounds were produced; in fact, two different hydroxy-compounds were isolated from each base, but from neither base

was there obtained a dinitrodiphenol identical with that described by Kunze (*Ber.*, 1888, **21**, 3331; compare also Schütz, *ibid.*, p. 3530), namely:



prepared by nitrating 4:4′-diphenol, or that discovered by Goldstein (*J. Russ. Phys. Chem. Soc.*, 1874, **6**, 193; 1878, **10**, 318) by oxidising *o*-nitrophenol, the constitution of which is not known.* From each base was obtained a compound having the composition of a dinitro-4:4′-diphenol and one having the composition of a tetranitrodihydroxybenzerythrene, the latter evidently having been produced by the coalescence of two diphenyl nuclei as in the case of the experiments mentioned above; they were easily separated by means of alcohol, but only one of the four compounds melted below 300°.

Experimental.

I.—*Derivatives of* 3:3′- *and* 3:5′-*Dinitrobenzidine.*

3:3′-*Dinitrodiformylbenzidine*, prepared by heating the base with anhydrous formic acid, is very soluble in nitrobenzene, and separates from acetic acid in brownish-yellow crystals, melting at 188°:

0·2596 gave 38 c.c. N_2 at 21° and 761 mm. N = 17·09.

$C_{14}H_{10}O_6N_4$ requires N = 16·97 per cent.

3:5′-*Dinitrodiformylbenzidine* separates from nitrobenzene in golden-yellow crystals, melting and decomposing at 282°:

0·1054 gave 15·2 c.c. N_2 at 19° and 759 mm. N = 16·97.

$C_{14}H_{10}O_6N_4$ requires N = 16·97 per cent.

A mixture of the above two compounds melted at 260°.

Dibenzoyl-3:3′-*dinitrobenzidine*, prepared by heating the base with benzoyl chloride, separates from nitrobenzene in yellow crystals, melting at 290°:

0·2719 gave 26·6 c.c. N_2 at 17° and 761 mm. N = 11·63.

$C_{26}H_{18}O_6N_4$ requires N = 11·62 per cent.

Dibenzoyl-3:5′-*dinitrobenzidine* crystallises from nitrobenzene in golden-yellow needles, melting at 298°:

0·1691 gave 17 c.c. N_2 at 21° and 760 mm. N = 11·77.

$C_{26}H_{18}O_6N_4$ requires N = 11·62 per cent.

A mixture of the above two compounds melted at 270°.

* Experiments are in progress with the object of elucidating the constitution of this compound.

3 : 3′-*Dinitro-4 : 4′-disucciniminodiphenyl*,

$$\begin{matrix}CH_2\cdot CO\\ |\\ CH_2\cdot CO\end{matrix}\!\!>N\cdot C_{12}H_6(NO_2)_2\cdot N<\!\!\begin{matrix}CO\cdot CH_2\\ |\\ CO\cdot CH_2\end{matrix},$$

was prepared by heating 3 : 3′-dinitrobenzidine with succinic anhydride at 150—160° for six hours. The alcoholic extract of the product furnished bright yellow crystals, melting at 203°:

0·0824 gave 9·1 c.c. N_2 at 18° and 763 mm. N = 13·00.
$C_{20}H_{14}O_8N_4$ requires N = 12·78 per cent.

3 : 5′-*Dinitro-4 : 4′-disucciniminodiphenyl*, prepared similarly at 140°, is insoluble in alcohol or benzene, but separates from nitrobenzene in yellow crystals, melting at 238°:

0·1016 gave 11·1 c.c. N_2 at 15° and 760 mm. N = 12·93.
$C_{20}H_{14}O_8N_4$ requires N = 12·78 per cent.

3 : 3′-*Dinitrophthalylbenzidine*, $C_6H_4<\begin{matrix}CO\cdot NH\cdot C_6H_3\cdot NO_2\\ |\\ CO\cdot NH\cdot C_6H_3\cdot NO_2\end{matrix}$. — This compound is formed when molecular proportions of phthalic anhydride and 3 : 3′-dinitrobenzidine are boiled in aqueous suspension for seven to eight hours. The orange-yellow product was crystallised first from dilute alcohol, and then from nitrobenzene, when it melted at 297—298°:

0·1124 gave 13·4 c.c. N_2 at 21° and 767 mm. N = 13·96.
$C_{20}H_{12}O_6N_4$ requires N = 13·86 per cent.

The substance is also formed when 3 : 3′-dinitrobenzidine and phthalic anhydride (2 mols.) are heated together at 140—150° for four hours (Found, N = 14·00. Calc., N = 13·86 per cent.).

4 : 4′-*Diphthalimino-3 : 5′-dinitrodiphenyl*,*

$$C_6H_4<\!\!\begin{matrix}CO\\ CO\end{matrix}\!\!>N\cdot C_{12}H_6(NO_2)_2\cdot N<\!\!\begin{matrix}CO\\ CO\end{matrix}\!\!>C_6H_4.$$

—When 3 : 5′-dinitrobenzidine was boiled in aqueous suspension with phthalic anhydride, no action took place even after two days, but on heating the materials at 140—150° for four hours, interaction occurred. The product was crystallised from nitrobenzene, and was found to consist of a mixture of a greyish-yellow substance (m. p. 265°), of which the amount formed was not sufficient for analysis, and canary-yellow crystals; the latter, which did not melt at 305°, were specifically lighter than the former, and mechanical separation was effected by means of benzene:

0·1582 gave 14·7 c.c. N_2 at 22° and 761 mm. N = 10·78.
$C_{28}H_{14}O_8N_4$ requires N = 10·48 per cent.

* The corresponding compound from 3 : 3′-dinitrobenzidine, which was analysed by Bandrowski (*Monatsh.*, 1887, **8**, 472), separates from nitrobenzene in pale yellow crystals melting at 284°; Bandrowski did not give the melting point.

4 : 4′-*Di*(3 : 6-*dichloro*)*phthalimino*-3 : 3′-*dinitrodiphenyl*,

$$C_6H_2Cl_2{<}{}^{CO}_{CO}{>}N\cdot C_{12}H_6(NO_2)_2\cdot N{<}{}^{CO}_{CO}{>}C_6H_2Cl_2,$$

was prepared by heating a mixture of 3 : 6-dichlorophthalic anhydride and 3 : 3′-dinitrobenzidine at 100—135° for four to five hours. The product was extracted with alcohol, and the greyish-yellow residue, which was soluble in benzene, melted at 191—192°:

0·1103 gave 8·1 c.c. N_2 at 19° and 760 mm. N = 8·58.

$C_{28}H_{12}O_8N_4Cl_4$ requires N = 8·30 per cent.

4 : 4′-*Di*(3 : 6-*dichloro*)*phthalimino*-3 : 5′-*dinitrodiphenyl* was prepared by heating a mixture of 3 : 6-dichlorophthalic anhydride and 3 : 5′-dinitrobenzidine at 150—160° for four hours. The product was extracted with alcohol, and the residue dissolved in benzene; on adding alcohol to the solution, a gelatinous, pale grey substance separated, which melted at 205° after turning yellow and shrinking at about 184°:

0·1377 gave 10·0 c.c. N_2 at 17·5° and 763 mm. N = 8·56.

$C_{28}H_{12}O_8N_4Cl_4$ requires N = 8·30 per cent.

(3 : 4 : 5 : 6-*Tetrachloro*)*phthalyl*-3 : 3′-*dinitrobenzidine*,

$$C_6Cl_4{<}{}^{CO\cdot NH\cdot C_6H_3\cdot NO_2}_{CO\cdot NH\cdot C_6H_3\cdot NO_2},$$

was obtained by heating 3 : 3′-dinitrobenzidine with tetrachlorophthalic anhydride (2 mols.) at 100—130° for four hours. The product, after extraction with alcohol and then with benzene, separated from nitrobenzene in yellow crystals, melting at 312°:

0·1798 gave 16·5 c.c. N_2 at 20° and 760 mm. N = 10·69.

$C_{20}H_8O_6N_4Cl_4$ requires N = 10·33 per cent.

(3 : 4 : 5 : 6-*Tetrachloro*)*phthalyl*-3 : 5′-*dinitrobenzidine*, similarly prepared from 3 : 5′-dinitrobenzidine, crystallises in pale yellow needles, which do not melt at 310°:

0·2211 gave 19·8 c.c. N_2 at 24° and 767 mm. N = 10·40.

$C_{20}H_8O_6N_4Cl_4$ requires N = 10·33 per cent.

A mixture of this and the preceding compound melted at 270°.

Azo-derivatives.

3 : 3′-*Dinitrodiphenyl*-4 : 4′-*bisazophenol*,*

$$HO\cdot C_6H_4\cdot N_2\cdot C_{12}H_6(NO_2)_2\cdot N_2\cdot C_6H_4\cdot OH,$$

prepared by adding a diazotised solution of the base to an alkaline solution of phenol, separates from xylene as a reddish-brown powder melting at 240—245°.

* Estimations of nitrogen in this and the three following compounds gave results from 0·6 to 1·8 below the calculated percentage, evidently due to the extreme difficulty in burning them.

3:5′-Dinitrodiphenyl-4:4′-bisazophenol, $C_{24}H_{16}O_6N_6$, separates from acetic acid as a black, amorphous powder, melting and decomposing at 250—255°.

3:3′-Dinitrodiphenyl-4:4′-bisazo-β-naphthol, $C_{32}H_{20}O_6N_6$, is a bright red powder insoluble in the usual organic solvents. It melts and decomposes at about 297° with previous sintering.

3:5′-Dinitrodiphenyl-4:4′-bisazo-β-naphthol is a black powder, very sparingly soluble in xylene, which does not melt at 335°. The diazotised bases were also combined with 1-naphthylamine-4-sulphonic acid (naphthionic acid) and with 8-amino-1-naphthol-3:6-disulphonic acid (H-acid) in order to obtain soluble bisazo-colouring matters, the shades of which on cotton could be compared.

The colouring matter from 3:3′-dinitrobenzidine and naphthionic acid dyes cotton in reddish-violet shades resembling those produced by "Congo Corinth B," whilst the corresponding colouring matter from 3:5′-dinitrobenzidine produces a bluer shade on cotton, similar to that furnished by "Azo-violet." Both these dyeings are changed to red by mineral acids. With "H-acid," 3:3′-dinitrobenzidine gave a reddish-grey (similar to "Direct Grey B"), whilst 3:5′-dinitrobenzidine gave a greenish-grey.

II.—*The Diazo-reaction Applied to the Dinitrobenzidines: Synthesis of Derivatives of Benzerythrene.*

In these experiments the bases were dissolved in concentrated sulphuric acid, the solutions cooled in ice, diluted slightly with water until the base began to separate, and diazotised by adding sodium nitrite. The solution was then filtered, and treated in the usual way.

Chlorine.—The diazo-solution was poured on copper bronze and hydrochloric acid.

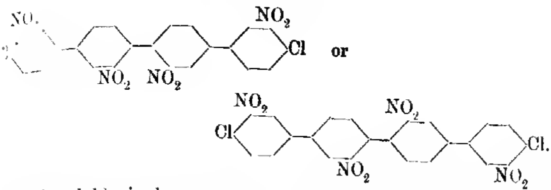
From 3:3′-dinitrobenzidine there was obtained *4:4′-dichloro-3:3′-dinitrodiphenyl*, which crystallises from glacial acetic acid in pale yellow needles melting at 111—112°:

0·1011 gave 7·7 c.c. N_2 at 18·5° and 764·3 mm. N = 8·9.

$C_{12}H_6O_4N_2Cl_2$ requires N = 8·9 per cent.

3:5′-Dinitrobenzidine, when similarly treated, gave *4″:4‴-dichlorotetranitrobenzerythrene* *:

* The ring system of benzerythrene has not yet been numbered. In Richter's "Lexikon" the name "4:4′-diphenylbiphenyl" is assigned to it. Neither this name nor "p-bisdiphenyl" appears to be suitable when substitution



which is soluble in benzene or glacial acetic acid, but insoluble in light petroleum or alcohol, and forms yellow crystals melting at 203°:

0·1082 gave 9·4 c.c. N_2 at 20° and 765 mm. N = 10·2.

$C_{24}H_{12}O_8N_4Cl_2$ requires N = 10·1 per cent.

In various preparations of this substance it was obvious that an azo-compound was simultaneously formed, as the values obtained in the estimation of nitrogen were often considerably higher than required by the above formula.

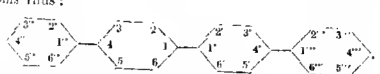
Bromine.—The products obtained in various experiments by treating the diazotised solution of 3 : 3′-dinitrobenzidine with hydrobromic acid and copper bronze or cuprous bromide all contained more nitrogen than was required by the expected dibromodinitrodiphenyl, or even by the corresponding derivative of benzerythrene, and evidently this was due to the presence of some azo-compound. 4 : 4′-*Dibromo*-3 : 3′-*dinitrodiphenyl* was, however, easily prepared by treating the diazotised solution with hydrobromic acid and bromine, and decomposing the perbromide formed in this way with glacial acetic acid (Saunders, *Amer. Chem. J.*, 1891, **13**, 486). It separates from glacial acetic acid in orange crystals melting at 137—138°:

0·1418 gave 8·6 c.c. N_2 at 23° and 765 mm. N = 7·0.

$C_{12}H_6O_4N_2Br_2$ requires N = 7·0 per cent.

The diazotised solution from 3 : 5′-dinitrobenzidine, when partly neutralised with sodium hydroxide and then treated with hydro-

...ducts are concerned. We therefore prefer to use "benzerythrene" and number ... carbon atoms thus:



...ther, in the absence of any direct chemical evidence (except as to the ortho-...sition of the nitro-groups) we have been compelled to refer to the two bases as ...3- and 3 : 5′-dinitrobenzidine (T., 1912, **101**, 2361; compare also this vol., ...). This being so we do not feel justified in assuming these positions in the ...erythrene compounds, as an additional complication is introduced as indicated ... the two formulæ given.

bromic acid and copper powder, yielded 4″:4‴-*dibromotetranitrobenzerythrene*, which is soluble in benzene or alcohol, and separates from the latter solvent in greyish-yellow crystals melting and decomposing at 184°:

0·1218 gave 9·4 c.c. N_2 at 30° and 762 mm. N=8·7.

$C_{24}H_{12}O_8N_4Br_2$ requires N=8·7 per cent.

This formula was confirmed by an estimation of bromine. By treating the diazotised solution of 3:5′-dinitrobenzidine with hydrobromic acid and bromine, and decomposing the perbromide formed with glacial acetic acid, 4:4′-*dibromo*-3:5′-*dinitrodiphenyl* was obtained. This separates from glacial acetic acid in orange-yellow crystals melting at 247°:

0·1603 gave 9·7 c.c. N_2 at 20° and 759 mm. N=7·0.

$C_{12}H_6O_4N_2Br_2$ requires N=7·0 per cent.

Cyanogen.—The diazotised solution prepared from 3:3′-dinitrobenzidine was partly neutralised with sodium hydroxide, and treated in the usual manner with cuprous cyanide. 3:3′-*Dinitro*-4:4′-*dicyanodiphenyl*, which was extracted from the product by means of benzene, separates from this solvent as a brown powder melting and decomposing at 190—192°:

0·1322 gave 22·2 c.c. N_2 at 29° and 762 mm. N=19·0.

$C_{14}H_6O_4N_4$ requires N=19·0 per cent.

This nitrile, when hydrolysed, furnishes an acid, which, however, could not be obtained in a pure state.

3:5′-Dinitrobenzidine, when similarly treated, gave 4″:4‴-*dicyanotetranitrobenzerythrene*, which is insoluble in ether, benzene, or alcohol, but dissolves in glacial acetic acid, and separates, on diluting the solution with water, as an amorphous, yellow powder, melting and decomposing at 195—198°:

0·0944 gave 12·5 c.c. N_2 at 22° and 767·2 mm. N=15·5.

$C_{26}H_{12}O_8N_6$ requires N=15·7 per cent.

Hydrolysis of this nitrile furnished an acid, which could not be obtained in a pure state.

Iodine.—3:3′-Dinitrobenzidine gave, on diazotisation and treatment of the solution with potassium iodide, 4:4′-*di-iodo*-3:3′-*dinitrodiphenyl*, which crystallises from dilute alcohol in yellow needles melting at 151—152°:

0·2342 gave 11·45 c.c. N_2 at 11° and 754·6 mm. N=5·8.

$C_{12}H_6O_4N_2I_2$ requires N=5·6 per cent.

3:5′-Dinitrobenzidine gave 4:4′-*di-iodo*-3:5′-*dinitrodiphenyl*, which is soluble in glacial acetic acid, alcohol, or xylene, but insoluble in acetone or benzene, and forms yellow crystals melting at 252—253°:

0·2010 gave 10·7 c.c. N_2 at 24° and 762 mm. N = 6·1.

$C_{12}H_6O_4N_2I_2$ requires N = 5·6 per cent.

Thiocyano-group.—The diazotised solution prepared from 3 : 3′-dinitrobenzidine was treated with sodium acetate until little mineral acid was present, and then poured into aqueous potassium thiocyanate. The *3 : 3′-dinitro-4 : 4′-dithiocyanodiphenyl* separated from alcohol in very pale, brick-red crystals, melting at 158°:

0·1028 gave 13·5 c.c. N_2 at 15° and 768 mm. N = 15·74.

$C_{14}H_6O_4N_4S_2$ requires N = 15·64 per cent.

3 : 5′-Dinitrobenzidine, when treated in the same way, gave *...dinitro-4″ : 4‴-dithiocyanobenzerythrene*, which separates from nitrobenzene as a yellow powder decomposing at 301°:

0·1668 gave 19·7 c.c. N_2 at 18° and 770 mm. N = 14·04.

$C_{26}H_{12}O_8N_6S_2$ requires N = 14·00 per cent.

Hydroxyl.—When the two dinitrobenzidines are diazotised and the solutions boiled, minute amounts of phenolic substances are formed, the main products being brown, amorphous, insoluble substances. By adding the diazotised solution from 3 : 3′-dinitrobenzidine to a boiling mixture of a solution of sodium sulphate and sulphuric acid (Eng. Pat. 7233 of 1897), a yellowish-brown, amorphous substance was obtained, which was soluble in sodium hydroxide. A portion of this dissolved in alcohol, but did not melt below 300°. Analysis indicated that the substance had the composition of a *3 : 3′-dinitro-4 : 4′-diphenol*, but its amorphous and infusible condition indicates that it possesses a higher molecular weight than that calculated from the simple formula:

0·1523 gave 13·7 c.c. N_2 at 22° and 757 mm. N = 10·38.

$(C_{12}H_8O_6N_2)_x$ requires N = 10·14 per cent.

The alcoholic filtrate from the above, on evaporation, yielded a brown, amorphous substance melting at 105°, which had the composition of a *3 : 3′-dinitro-4 : 4′-diphenol* combined with water:

0·3055 gave 24·0 c.c. N_2 at 17° and 761 mm. N = 9·26.

0·2571 lost 0·0170 at 110—120°. H_2O = 6·19.

$C_{12}H_8O_6N_2,H_2O$ requires N = 9·52; H_2O = 6·12 per cent.

The anhydrous substance decomposed at 200—205°.

The part of the above-mentioned yellowish-brown substance which did not dissolve in alcohol (or glacial acetic acid) did not melt at 310°:

0·1646 gave 14·35 c.c. N_2 at 23° and 761 mm. N = 10·08.

$(C_{12}H_8O_6N_2)_x$ requires N = 10·14 per cent.

This substance has thus the composition of a *3 : 3′-dinitro-4 : 4′-diphenol* of high molecular weight.

On decomposing the diazo-solution with a boiling solution of copper sulphate (D.R.-P. 167211), the product was only partly soluble in sodium hydroxide; the soluble portion furnished the hydrated compound melting at 105°, described above.

The above reactions were repeated with 3:5′-dinitrobenzidine, and a third reaction, which consisted in adding the diazo-solution to hot concentrated sulphuric acid, was also carried out. From each of the three experiments a very small amount of a substance soluble in sodium hydroxide was obtained, the main product being brown, amorphous, and insoluble. The material soluble in alkali separated from dilute acetic acid as a yellow powder, which was apparently identical with the 3:5′-dinitro-4:4′-diphenol obtained by the action of light on diazotised 3:5′-dinitrobenzidine (see below).

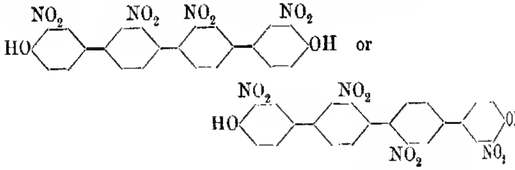
Action of Light on the Diazo-solutions.

The diazotised solutions were submitted to the action of sunlight at the ordinary temperature until decomposition was complete (Orton, Coates, and Burdett, *loc. cit.*). The precipitates formed from each solution were soluble in sodium hydroxide, and were separated by means of alcohol into two portions, one being soluble and the other insoluble in this solvent. In the case of 3:3′-dinitrobenzidine, decomposition was complete in two weeks and there were obtained a 3:3′-*dinitro-4:4′-diphenol*, which did not melt at 300°, and was soluble in alcohol:

0·1192 gave 10·4 c.c. N_2 at 23° and 764 mm. N = 10·1.

$(C_{12}H_8O_6N_2)_x$ requires N = 10·1 per cent.

and a *tetranitro-4″:4‴-dihydroxybenzerythrene*,



which did not melt at 330°, and was insoluble in alcohol:

0·2042 gave 19·5 c.c. N_2 at 19° and 763 mm. N = 11·2.

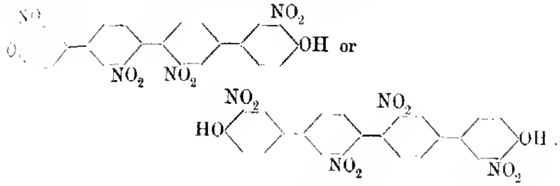
$C_{24}H_{14}O_{10}N_4$ requires N = 10·8 per cent.

Both the above substances were brown and amorphous.

In the case of 3:5′-dinitrobenzidine, decomposition was complete in three weeks, and there were obtained a 3:5′-*dinitro-4:4′-diphenol*, which separated from glacial acetic acid or alcohol as a brown, amorphous substance, melting at about 180°:

...gave 10·35 c.c. N_2 at 19·5° and 763 mm. N = 10·5.
$C_{12}H_8O_6N_2$ requires N = 10·1 per cent.,

...*tetranitro-4'' : 4'''-dihydroxybenzerythrene*,



...brown, amorphous substance, which did not melt at 330°, and ... insoluble in alcohol:

...gave 15·35 c.c. N_2 at 25° and 770 mm. N = 10·8.
$C_{24}H_{14}O_{10}N_4$ requires N = 10·8 per cent.

Whether this substance was identical or not with that described ... could not be ascertained owing to their infusible nature.

The expenses of this work have been partly defrayed by grants from the Chemical Society and the Royal Society, for which the authors desire to express their grateful thanks.

21, AYLESTONE AVENUE,
BRONDESBURY PARK,
LONDON, N.W.

HACKNEY TECHNICAL INSTITUTE,
LONDON, N.E.

CXXI.—*Absorption Spectra and Chemical Reactivity. Part III. Trinitrobenzene, Trinitroanisole, and Picric Acid.*

By EDWARD CHARLES CYRIL BALY and FRANCIS OWEN RICE.

...their previous papers (T., 1912, **101**, 1469, 1475; this vol., 91) the general theory was put forward that any molecule of a substance in the free state is the centre of a closed field due to the condensing together of the force lines arising from the free affinities of the individual atoms within the molecules. It was shown ... these condensed fields may be unlocked or opened by their interpenetration by the force lines arising from the residual affinity of the molecules of a second substance when the two are mixed. By the residual affinity is meant the balance of free affinity after the maximum possible condensation has taken place. Loose systems between the molecules are formed in this way, which

correspond with the solvates formed when substances exist in solution.

In considering the mechanism by which the closed force field of any one molecule is opened by the residual affinity of a second substance, it is evident, in the first place, that there must exist a difference between the two. As a general statement it may be said that in order that a substance may have its closed field opened it must be treated with a second substance, which differs in character, and the greater the difference in character the more will the force field be opened. The point of attack may vary with the nature of the compound, and, of course, in some cases the same compound will be opened both by a strong acid and by a strong base, the nature of the opening being different in the two cases. Such a compound is amphoteric in the real sense of the term, and the correct definition of an amphoteric substance is a compound of such a type that its closed force field is opened differently by an acid and by a base.

In the second place, it follows from the general conception that the opening up process will be carried out in stages. This was emphasised in a previous paper dealing with the application of the theory to fluorescence (T., 1912, **101**, 1469). Whereas previously only two of the stages had been recognised in the opening up, we have now succeeded in studying the process more completely, and in recognising several distinct stages.

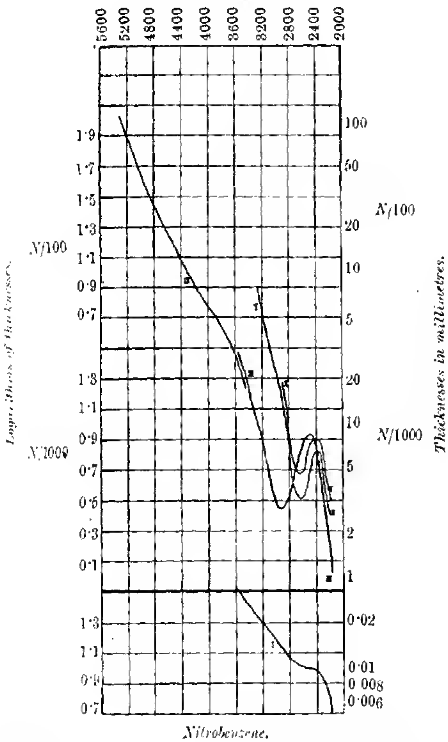
One point of interest at once arises from the existence of the various stages in the opening up of the closed force fields. The evidence of experiment clearly shows that these stages possess a separate and distinct existence, and are stable under the necessary conditions. They represent the same substance with different free energy contents, since the greater the amount of condensation which takes place between the force lines the greater the free energy that escapes. In order, therefore, to convert a substance from stage 1 (in which the maximum possible condensation exists) into stage 2, or first partly opened up condition, a definite quantity of free energy is required. In other words, free substances must necessarily take up energy in definite quanta, a conclusion that is of some importance in relation to Planck's energy quantum theory and photochemistry.

In the present paper we deal with the application of the theory to nitro-derivatives of benzene, and more particularly to trinitrobenzene, picric acid, and trinitroanisole. In previous papers (T., 1905, **87**, 1332; 1910, **97**, 591) it was pointed out that in nitrobenzene the affinities of the nitro-group and phenyl residues mutually influence one another in such a way that only a very small selective absorption is exhibited. It is a well-known fact that

the nitro-group in the aliphatic nitro-compounds and in the metallic nitrates tends to give powerful selective absorption, and the same is true of the phenyl residue in benzene and its homologues. In nitrobenzene, however, the free affinities of the two

FIG. 1.

Wave-lengths.



Nitrobenzene.

I. *Pure substance.*
II. *In alcohol.*
III. *In 80 per cent. sulphuric acid.*
IV. *In dimethylaniline.*
V. m-*Nitrobenzenesulphonic acid in 80 per cent. sulphuric acid.*

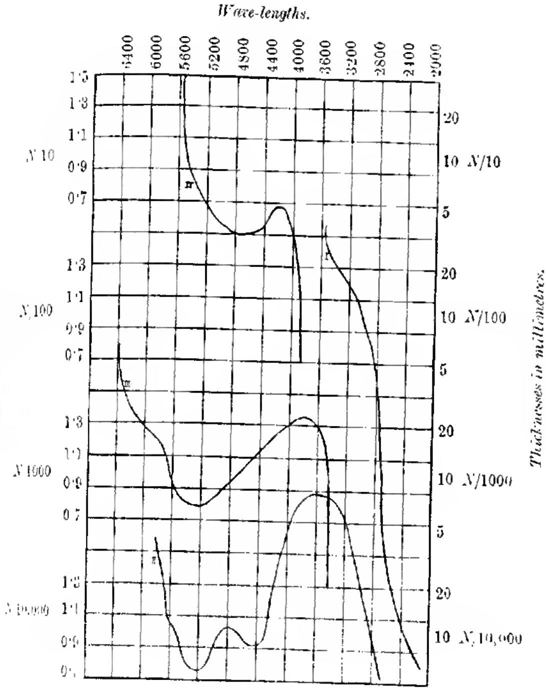
groups have condensed together to give a very stable system, which is not readily opened up by the ordinary solvents in the presence of light. A small absorption band is therefore exhibited by nitrobenzene in the ordinary solvents, which diminishes to a step-out

when the pure liquid is examined. Evidently, therefore, the free affinities of the nitro-group and the phenyl residue are of opposite character, and whilst that of the nitro-group is electronegative or acid in type, that of the phenyl group is of an electropositive or basic type. It is quite possible, however, to open up the system of nitrobenzene by the use of special solvents. It is an amphoteric substance in the strict sense of the word, for the closed system can be opened by solution either in moderately concentrated sulphuric acid (80 per cent.) or in dimethylaniline, and the absorption spectra in the two cases are different owing to the difference in the manner in which the nitrobenzene is opened up. The absorption curves of nitrobenzene in the pure state, in alcoholic solution, in 90 per cent. sulphuric acid solution, and in solution in dimethylaniline, are shown in Fig. 1, curves I, II, III, and IV.* Curve V is that of *m*-nitrobenzenesulphonic acid in 80 per cent. sulphuric acid, and shows from the difference between it and curve III that the nitrobenzene is not sulphonated in the 80 per cent. sulphuric acid solution. The absorption curve of the dimethylaniline solution does not exhibit any definite absorption band, but shows evidence of considerable absorption of the visible rays of the spectrum. It is obvious from these curves that a very profound modification is brought about in the nitrobenzene by solution in these two solvents. It is amphoteric in the sense that its closed force field is differently attacked by a strong acid and a strong base. As was stated above, owing to the electropositive character of the phenyl nucleus and the electronegative character of the nitro-group, nitrobenzene forms a very completely closed system which is opened to a very small degree by solution in alcohol. If now trinitrobenzene be considered, this compound, owing to the two additional nitro-groups, is much more electronegative or acid in character than nitrobenzene. The closed force field is not opened by alcohol, and the solution in this solvent shows no absorption band at all (Fig. 2, curve I). On the other hand, the closed system is extremely easily opened by basic solvents, and here the results obtained are of considerable interest. As is well known, the addition of sodium ethoxide to the alcoholic solution develops a fine red colour, and the absorption spectrum is shown in Fig. 2, curve II, which gives the absorption curve of a trinitrobenzene in the presence of $N/10$-sodium ethoxide. Almost identical absorption is shown by

* Whereas in all previous papers the absorption curves have been drawn in terms of oscillation frequencies ($1/\lambda$), all the curves in this paper are drawn in terms of wave-lengths. This change has been adopted in response to a direct request from Professor Kayser. Professor Kayser, who is a member of the International Committee on Wave-length Standards, has advised us that the expression of all measurements of absorption in terms of wave-lengths is much to be preferred.

trinitrobenzene in piperidine solution, the difference between the two curves being very slight. In each case two absorption bands are shown, and therefore light vibrations of two frequencies are absorbed under these conditions, and evidently, therefore, two differing amounts of free energy are being absorbed simultane-

FIG. 2.



Trinitrobenzene.

I. *In alcohol.*
II. *In sodium ethoxide.*
III. *In dimethylaniline.*
IV. *In benzene and anthracene.*

ously. It follows from this that two different stages in the opening-up process of trinitrobenzene are produced by the action of sodium ethoxide and by piperidine. The absorption of trinitrobenzene in dimethylaniline solution is shown in Fig. 2, curve III, and again there are evidences of two stages in the opening-up of its closed ... One very marked absorption band is shown, and a

step-out at greater wave-length, which shows that another stage is also brought into play. It is interesting to note that the more refrangible absorption band of the dimethylaniline solution is the same as the less refrangible band of the piperidine solution, so that one stage in the opening-up is common to both solutions. We have therefore altogether three distinct stages in the opening up of the closed system of trinitrobenzene, two of which are brought about by solution in alcoholic sodium ethoxide and in piperidine, and two by solution in dimethylaniline, and middle stage being common to all the solvents.

The fact that trinitrobenzene possesses such a well-marked closed system due to the opposite affinities of the nitro-groups and the phenyl residue, at once suggests the use of complex aromatic hydrocarbons for purposes of opening up the closed system. In Fig. 3, curve IV, is shown the absorption curve of trinitrobenzene in solution in benzene previously saturated with anthracene. One broad absorption band is here shown, and clearly covers the same wave-lengths as the two bands shown by the piperidine solution and by the solution in alcoholic sodium ethoxide. The result of these investigations is that three separate and distinct stages have been recognised in the opening up of the closed system of trinitrobenzene. The first of these is obtained by solution either in piperidine or in alcoholic sodium ethoxide. The second stage is obtained by solution either in piperidine, alcoholic sodium ethoxide, or dimethylaniline. The third is only obtained in dimethylaniline solutions. When dissolved in the benzene–anthracene mixture, both the first two phases also co-exist. The wave-lengths of the light absorbed by the three stages are approximately 430 $\mu\mu$, 515 $\mu\mu$, and 600 $\mu\mu$.

It is well known that trinitrobenzene tends to form compounds with sodium ethoxide and with anthracene and the complex aromatic hydrocarbons generally. We venture to think that our observations afford an explanation as to why these compounds are formed. When a compound possessing a closed field is mixed with another compound possessing residual affinity of an opposite type, the closed system is opened by being interpenetrated by the force lines arising from the residual affinity of the second substance. If now the difference between the properties of the two compounds be sufficiently marked, the system formed will be found to possess characteristic properties of its own as regards solubility in an indifferent solvent, etc. In the case of trinitrobenzene and anthracene, for example, the difference between their properties is sufficiently great for the system formed between the two to be relatively stable in alcoholic solution. If strong alcoholic solutions of the two be mixed, therefore, a "compound" separates out. In

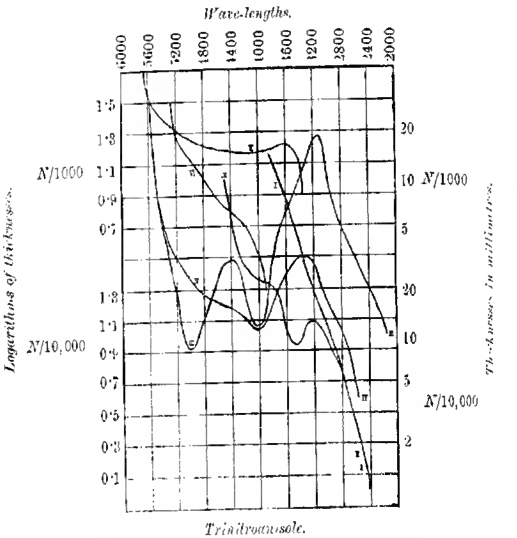
the general case the stability of this compound depends on the difference in properties between the reacting substances. Such a compound has only a stable existence when this difference is well marked, but the spectroscope is able to detect the mutual influence of the two substances when the difference in their properties is far too small to produce a stable compound of the two. When the difference between the properties of the two reacting substances is increased, the resulting compound becomes more and more stable until finally we arrive at salt formation. There is therefore no need to conceive of any break in continuity between the simple mutual influence between two substances which can only be detected optically and the formation of a salt between acid and base. The spectroscope would seem, therefore, to afford a far more delicate method of detecting the formation of loose additive compounds or their tendency to form, than the other physical methods such as those used by Kremann.

These observations also give an explanation of the nitration of aromatic hydrocarbons. Owing to the mutual influence of the nitro-group and the benzene ring, the nitric acid opens up the closed field of the hydrocarbon, with the result that a loose additive compound of the two is formed, which then proceeds to rearrange itself, giving water and the nitro-compound. The process is exactly analogous to the sulphonation of aromatic compounds, which has already been investigated by us, and in which the intermediate phase was observed (T., 1912, **101**, 1475). The formation of additive compounds with trinitrobenzene and aromatic hydrocarbons is quite analogous to the first stage in the nitration reaction, when the nitric acid and aromatic substance form a loose additive compound.

We have also examined trinitroanisole, and the results are somewhat similar to those obtained with trinitrobenzene. The absorption curves are shown in Fig. 3, where I is that obtained with a freshly-prepared solution of the recrystallised colourless compound in alcohol. This curve does not agree with that observed by Buttle and Hewitt (T., 1908, **95**, 1755), and is very similar to that of trinitrobenzene in the same solvent. The curve given by Buttle and Hewitt lies nearer to the red than ours, and the reason of this will be explained below. The addition of sodium ethoxide to the alcoholic solution at once produces a fine red colour, and the absorption spectrum is now shown by curve III in Fig. 3. Two bands are shown here, which closely approximate to the two bands obtained with trinitrobenzene under the same conditions. The solution of trinitroanisole in piperidine is also strongly coloured, and its absorption is shown by curve IV in Fig. 3. The more refrangible absorption band of the alcoholic sodium ethoxide

solution is also evidenced here, whilst the less refrangible band is reduced to a step-out. The difference in these absorption curves shows that trinitroanisole is less easily opened up than trinitrobenzene. This is more strikingly shown by the absorption exhibited by the solution in dimethylaniline and in the benzene–anthracene mixture. In the case of trinitrobenzene very well marked absorption bands are shown, but with trinitroanisole there is evidence of much less absorption (curves V and VI, Fig. 3). The dimethylaniline solution of trinitroanisole shows only a very shallow band,

FIG. 3.



I. *In alcohol (fresh).*
II. *In alcohol after exposure to light.*
III. *In sodium ethoxide.*
IV. *In piperidine.*
V. *In dimethylaniline.*
VI. *In benzene and anthracene.*

which, however, resembles the bands given by trinitrobenzene in that it extends over the same wave-lengths as the absorption bands of the alcoholic sodium ethoxide solution. The benzene–anthracene solution also shows evidences of absorption over the same region, but the band has given place to a very shallow step-out.

When trinitroanisole has been kept for some time, it becomes yellow, but may be obtained colourless after recrystallisation. The existence of two forms with the same melting point seems already to have been recognised (Hantzsch, *Ber.*, 1906, **39**, 1084), and it

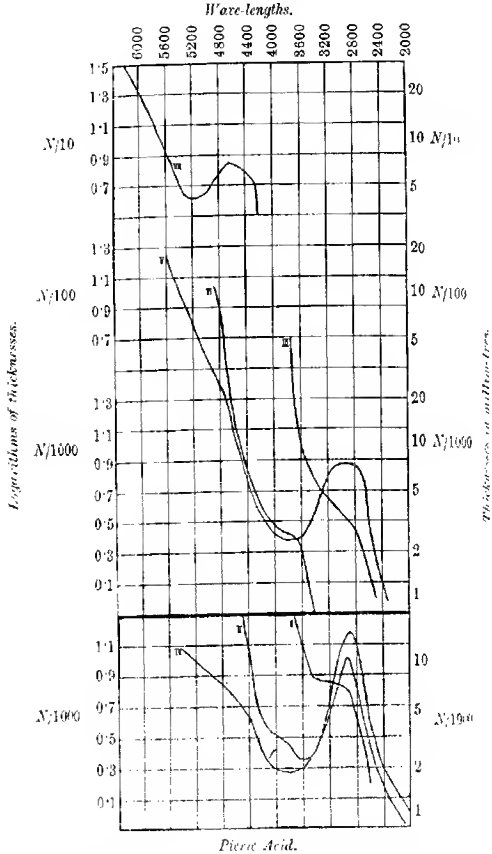
is interesting to note that the two forms have different absorption spectra. If the freshly prepared colourless solution in alcohol is kept, especially if left in the light, it turns strongly yellow, and the absorption spectrum is shown by curve II, Fig. 3. There is now one well-marked absorption band at a wave-length of 360 $\mu\mu$, and there is, moreover, a step-out or incipient absorption band over the same region as the more refrangible band of the piperidine and alcoholic sodium ethoxide solutions. It may be said here that this form gives the same absorption spectrum, on the addition of sodium ethoxide, as the colourless form, which proves at once that the formation of the yellow colour is not due to hydrolysis. Altogether, therefore, there are three absorption maxima with trinitroanisole, and this substance is thus capable under suitable conditions of absorbing three different quantities of free energy. Four different phases of this compound must therefore be capable of existence according to the amount of free energy that is supplied to it. The colourless solid variety is that form in which the maximum possible condensation has taken place in the force field surrounding the molecules. By supplying free energy to this, three other forms can be produced, and represent different stages in the opening up of this closed system. The wave-lengths of the light absorbed by the three opened up phases, and which are characteristic of them, are 510 $\mu\mu$, 410 $\mu\mu$, and 360 $\mu\mu$.

If the alcoholic solution of the colourless modification is kept exposed to light for a short time until it is coloured faintly yellow, that is to say, until only a relatively small fraction has been converted to the yellow form, then the absorption curve is shifted a little towards the red at the greater concentrations. The curve then agrees with that given by Buttle and Hewitt, and already noted. There is no doubt, therefore, that Buttle and Hewitt's observations referred to a solution containing a small quantity of the yellow or partly opened up form of trinitroanisole.

Picric acid differs from trinitroanisole in that it is still less readily opened up by alkaline solvents. The absorption curves of this compound are shown in Fig. 4, where curve I is that of picric acid in heptane, II in alcohol, III in alcoholic hydrogen chloride, IV in concentrated sodium hydroxide, V in piperidine, VI in dimethylaniline, VII in benzene containing anthracene. The two first curves are those given by the colourless and yellow modifications of picric acid, and we may point out the close resemblance between the form of the absorption curves given by the latter and that given by the yellow form of trinitroanisole (curve II, Fig. 2). The same conclusion is therefore to be drawn as to these two modifications of picric acid as in the case of trinitroanisole. The colourless variety is the completely closed form, whilst the yellow form, containing more

free energy, is the first stage in the opening up of the closed form. Hantzsch attributes the *aci*-constitution to this yellow form, but

FIG. 4.



Picric Acid.

I. *In heptane.*
II. *In alcohol.*
III. *In alcoholic* HCl.
IV. *In concentrated* NaOEt.
V. *In piperidine.*
VI. *In dimethylaniline.*
VII. *In benzene and anthracene.*

we would point out that this view is untenable, inasmuch as exactly the same phenomenon holds in the case of trinitroanisole, where the *aci*-form is ruled out.

An interesting fact about picric acid is the readiness with which it gives the yellow form in alcoholic solution compared with trinitroanisole, whereas the latter gives at first a colourless solution in alcohol, which under the influence of light passes into the yellow form; the former at once gives the yellow form, or first stage in the opening up, in alcohol.

When an alcoholic solution of picric acid is treated with sodium ethoxide in equivalent quantities, no change in the absorption is noticed, as already pointed out by Buttle and Hewitt. They attribute this to the fact that the salt will be so strongly ionised that the absorption will be that of the picric ion. The ionisation will, however, be much less in alcoholic solution, and yet even here no change is observed on the addition of an equivalent of sodium ethoxide. Buttle and Hewitt say, moreover, that in all probability the picric ion will be derived from the *aci*-form, and therefore the absorption would in that case be that of the *aci*-form. When, however, a very concentrated solution of sodium hydroxide is used as solvent for the picric acid, the absorption is changed, for signs of a new absorption band begin to make their appearance over the same region as the band given by picric acid dissolved in the benzene-anthracene mixture. Now undoubtedly this absorption is due to the undissociated sodium salt, and if the absorption of the solution with one equivalent of sodium ethoxide is due to the *aci* or quinonoid ion, to what is the incipient new band due? This incipient band is given in less degree by a piperidine solution of picric acid, and very completely by the solution in the benzene-anthracene mixture. It appears that the conception of the *aci*-form is unable to explain the results. The same explanation is applicable here as in the case of trinitrobenzene and trinitroanisole. The various absorption bands are due to the existence of different stages in the opening up of the closed fields surrounding the picric acid molecule, each stage being characterised by an absorption band. As picric acid shows evidences of two absorption maxima, so two different stages in the opening up are present in equilibrium in this solution. Then again there is the more completely opened up form which is readily obtained in solution in the benzene-anthracene mixture, and much less readily in solution in concentrated sodium hydroxide or in piperidine. Altogether, therefore, we have to recognise the existence of four phases of picric acid. First, the colourless or completely closed form; secondly, the two forms which co-exist in alcoholic solution and in solution in strong sodium hydroxide; and finally the fourth form, which exists in greatest amount in solution in the benzene-anthracene mixture. The absorption maxima characteristic of the three last forms are approximately 359 $\mu\mu$, 408 $\mu\mu$, and 516 $\mu\mu$. The last phase

is the most completely opened up condition of picric acid yet obtained.

The following table shows the various absorption maxima possessed by trinitrobenzene, trinitroanisole, and picric acid, and as the existence of each one marks a definite stage in the opening up of the closed force field, they represent the wave-lengths of the light energy absorbed by these forms:

	4.	3.	2.	1.
Trinitrobenzene	600	515	430	— $\mu\mu$
Trinitroanisole	—	510	410	360 $\mu\mu$
Picric acid..................	—	516	408	359 $\mu\mu$

The variations in the wave-lengths of the various maxima obtained with the three compounds is not large. It will be noticed that trinitrobenzene gives one maximum (600 $\mu\mu$), which the other two do not. This absorption maximum, as previously pointed out, is obtained with dimethylaniline as solvent, and corresponds with a more complete stage in the opening up than we have yet been able to observe in the case of the other two compounds. This fact agrees with what has already been pointed out, namely, that trinitrobenzene is most easily and picric acid least easily opened up by the three substances.

Since this paper was written, a communication by Clarke, Macbeth, and Stewart has been published (P., 1913, **29**, 161), in which they deal with the colours given by tetranitromethane with substances possessing various types and degrees of residual affinity. It would seem that these are due to similar phenomena, as described above, namely, the opening up of the closed system of the complex nitro-compounds by the force lines due to the various residual affinities with which it is treated.

In considering the absorption of light by any organic compounds it must be remembered that the light is doing work on the compound. When a solvent opens up the closed system of a solute and the mixture absorbs definite wave-lengths of light, this light is doing work, and increases the effect due to the solvent. The solvent alone brings about an equilibrium between the less closed and less opened phases, and the light when it is absorbed increases the effect of the solvent, that is to say, it shifts the equilibrium towards the more opened form. In other words, a photodynamic equilibrium is set up. This point of view was brought out in our previous paper (this vol., p. 91), where we showed that when the mass of solvent is increased beyond a certain limit the amount of light absorbed tends to decrease, and in the case of ethyl aceto-acetate it is easy to reach a dilution at which the light absorption vanishes. This phenomenon will be observed when the equilibrium is carried so far in one direction by the solvent that there is no

...k will for the light to do. Perhaps this may be made clearer by reference to a specific case, in which the light has actually been proved to do work. Certain cases have been observed in which the electrical conductivity, and hence the ionisation of a solution, is increased by light. The equilibrium between dissociated and undissociated molecules is shifted towards the side of dissociation by light. If such a solution were diluted until the ionisation were practically complete, then the amount of light absorbed would be very small indeed compared with that absorbed by an equimolecular layer of the stronger solution.

When the closed force field of a substance is opened up it absorbs free energy and becomes endowed with chemical reactivity. Again, when the system is entirely closed the reactivity is vanishingly small, and as the systems are opened up by the addition of definite quantities of free energy the reactivity is enhanced by definite amounts. In the cases where ionisation takes place the reactivity of the system is usually attributed to the ions, but it would seem preferable to consider that the reactivity is a property of the whole system, and that the formation of the ions is a phenomenon which is secondary in the sense that it is a function of the enhanced reactivity arising from the conditions under which the salt exists. This point of view has already been discussed for the cupric salts by Garrett (*Zeitsch. Elektrochem.*, 1913, **19**, 1).

THE UNIVERSITY, LIVERPOOL.

CCXII.—*The Fractionation of Alloys and Minerals in the Electric Micro-furnace.*

By ARNOLD LOCKHART FLETCHER.

THE following apparatus, for which the name "Micro-furnace" * is proposed, has been employed in the distillation at high temperatures of various inorganic substances, including alloys, minerals, and ores.

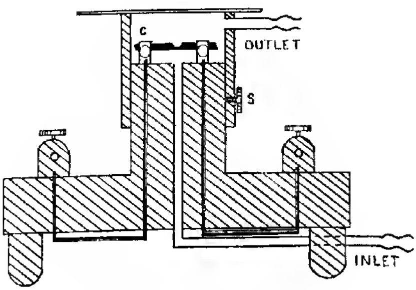
It consists of a brass drum sliding over a solid slate cylinder from 5 to 8 cm. in diameter, bearing a pair of terminals for a carbon rod,† which can be heated rapidly to extremely high temperatures by the passage of an electric current. These terminals

* For assistance in designing the most convenient form of this furnace, I am indebted to my father, Mr. G. Fletcher.

† Carbons of small sectional area suitable for the qualitative application of this instrument have been obtained from the Le Carbone Co., London.

are most conveniently made in the form of horizontal clock springs, which press the carbon down on a block of copper or graphite

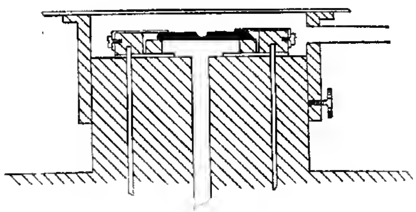
FIG. 1.



MICRO - FURNACE

resting on a copper strip connected to the terminals, as shown in Fig. 2. The carbon may be protected or partly enclosed when desirable by loose, closely placed parallel carbons. The general arrangement is shown below:

FIG. 2.



SUBLIMATION CHAMBER of MICRO-FURNACE

In the above figure the carbon rod and terminal connexions are for the sake of convenience placed diametrically, the terminals being shown turned through a right angle. In practice, however, they may be arranged with the carbon at right angles to the spring clips, forming with them three sides of a rectangle, thus reducing the size of the chamber. The sliding cylinder is covered by a receiving plate of glass, clear or opaque silica, or biscuit ware. The space surrounding the rod can be filled with various gases or rendered partially vacuous by means of inlet and outlet tubes, the former perforating the slate support, whilst the latter is fixed below the upper rim of the brass cylinder. The spring clips holding the rod are easily manipulated during the frequent

... of the carbon by removing for a moment the sliding ... This drum may be set in any position on the slate cylinder by means of the screw S, and thus the size of the chamber, and the distance between the carbon and cover plate, regulated at will. The inlet tube which opens under the heated particle tends to transport heavy vapours to the receiving plate.

Carbon appears to be the most satisfactory support for the material under examination because (a) it may be raised to the highest attainable temperatures, (b) it prevents oxidation when desirable, (c) it does not contain impurities likely to affect the analytical results, and does not usually combine with or adhere to the molten metal, and hence non-volatile residues may be removed for gravimetric purposes.

As examples of the application of this furnace to qualitative analysis, the following table is presented, showing the colours obtained in air on glass or transparent silica:

Family.	Element.	Deposit.
I.	Copper	red, green, yellow.
	Silver	dull grey, some pink.
	Gold	red, violet to purple, gold.
II.	Glucinum	white.
	Magnesium	white.
	Zinc	white.
	Cadmium	red-brown.
	Mercury	grey-white.
III.	Aluminium	white.
	Indium	pale yellow.
	Thallium	red and white.
	Titanium	white.
	Zirconium	cream.
	Cerium	white.
	Silicon	white, some yellow.
	Tin	white.
	Lead	yellow.
V.	Vanadium	yellow-green.
	Columbium	white.
	Tantalum	white.
	Arsenic	white.
	Antimony	white.
	Bismuth	yellow.
VI.	Chromium	green.
	Molybdenum	pale yellow.
	Tungsten	white.
	Uranium	black.
	Selenium	red.
	Tellurium	white.
VII.	Manganese	light brown.
VIII.	Iron	red-brown.
	Cobalt	black.
	Nickel	black.
	Ruthenium	grey.
	Platinum	black.

The following table represents the colour of deposits obtained ... the presence of hydrogen sulphide, (b) by distillation on a ... on which iodine has been previously sublimed:

Element.	Deposit in hydrogen sulphide.	Deposit on plate bearing iodine.
[illegible]	green-black	white.
[illegible]	black	pale yellow.
[illegible]	—	yellow-brown.
[illegible]	white	white.
Zinc	yellow	white.
...y	black	scarlet and yellow.
...	red-brown	yellow.
...	black, red and brown	orange-brown.
Tin	black and yellow	orange-brown.
Lead	blue-black	deep yellow.
Arsenic	red, yellow	deep yellow.
Antimony	red	orange-red.
Bismuth	brown, black	chocolate.
Selenium	red	black.
Tellurium	black	chocolate.

In dealing with refractory substances, such as steels and ... alloys, two difficulties were encountered: the decrepitation of the fusion at high temperatures, and the rapid burning of the carbon. The first of these may be overcome by placing strips of carbon or biscuit ware against the rod, so that the fusion is unable to escape, or by using larger carbons and heavier currents, and the second to some extent by using larger carbons partly protected. The rod should not be wholly embedded, as, in the absence of free oxygen, a deposit of carbon interferes with the distillation. For high temperature work the most suitable size of the rod ... from 8 to 30 sq. mm. cross-section. This is reduced at the centre according to the current available.

Quantitative Separations in Air.

The general behaviour of many metals when heated in depressions in the carbon of the micro-furnace in the manner described suggested the possibility of obtaining quantitative results by this method. From the experiments so far carried out, it appears that the micro-furnace is capable of yielding quantitative results with an accuracy which depends on the nature and relative quantities of the constituents of the alloy.* It has been recently shown (Turner, *J. Inst. Metals*, 1912, **12**, Jan., and Groves and Turner, T., 1912, **101**, 585) that quantitative separations may be carried out on certain alloys by heating for some time in a vacuum up to 1200° in the electric furnace. By the process to be described, the method may be extended to include in certain cases alloys which are stable at the temperature limits of the tube furnace. A small weighed filing—say, 4 or 5 milligrams—of the alloy is placed in the hollow of the carbon rod, which is then covered with a fragment of transparent silica, and the temperature of the strip is raised slowly until the deposition of one constituent is observed on the cover plate. The temperature is then steadied for a short time, until this has ceased, when the circuit is broken and the rod cooled. An inspection of the colour and nature of the deposit shows whether the constituent has volatilised *per se*. To aid this inspection a number of such deposits should first be prepared. This operation is then repeated as often as necessary, and the remaining globule weighed. This method possesses certain advantages over one in which the sublimate is weighed, and which therefore involves an assumption as to the chemical nature and uniform character of the deposit. A further heating will indicate whether the fractionation has been satisfactorily accomplished. If not, further weighings must be made. The final residue should be volatilised, as this method often reveals traces of unsuspected

When a separation is incomplete, a rough approximation to the proportions present may be made by inspection, or from readings taken at some points between the appearance of the second and disappearance of the first, constituent.

A quantitative separation can only be carried out in cases where the substances or their compounds with the surrounding atmosphere differ greatly in volatility. In practice, the following difficulties arise: (1) One constituent is mechanically retained by another, and is thus difficult to volatilise; thus, although tin and lead are partly separable, they are difficult to separate owing to the retention of lead inside the fusion. This is to some extent overcome by repeated heating and cooling, aided by intermediate turning of the soft fusion, whereby the lead is brought to the surface. (2) The alloy does not assume the spherical condition. This is often the case with alloys containing aluminium, which tends to powder. (3) Oxidation. When the sublimate oxidises freely it tends to transport portions of the residue. The presence of much oxide in the residue introduces an error into the calculation. In most cases this may be prevented by the use of large ...ons or by partly surrounding the rod with parallel graphite carbon rods; in others the separation should be carried out in ...rogen or coal gas.

There is in practice usually a tendency towards underestimating the residue, and this is enhanced as the volatilities of the substances under the conditions of the separation approximate; for example, copper and nickel are difficult to separate quantitatively. Analyses are in general most easily carried out in alloys in which the constituent most freely volatile is present in the smallest relative quantity. The micro-furnace will find its chief use as a powerful means for ascertaining rapidly what elements are present in any alloy, mineral or ore, and roughly in what proportions they are present.

The following is a list of alloys on which quantitative separations have been attempted:

Brass.

1. 0·0031 yielded after distillation of zinc a residue 0·0019. Cu 61·29.
2. 0·0049 „ „ „ „ 0·0030. Cu 61·23.

Brass (Cu, 64·32; Zn, 35·68; Ni, 2·85; Fe, 1·76).

1. 0·0073 yielded after distillation of zinc a residue 0·0050. Cu 68·49.
2. 0·0063 „ „ „ „ 0·0043. Cu 68·25.
3. 0·0058 „ „ „ „ 0·00395. Cu 68·10.

German Silver (Cu, 60; Ni, 15; Zn, 25).

A separation of copper and nickel is difficult owing to the approximation of their volatilities. There is, however, in the distillation of mixed copper and nickel a point at which there is in the deposit a marked decrease in the amount of copper and an increase in the quantity of nickel obtained. Traces of copper appear until the end. A rough approximation may be obtained if a weighing is made at this point.

1. 0·0029 yielded after distillation of zinc a residue 0·0021. { Zn 27·6,
   and ,, ,, ,, copper ,, 0·0004 { Cu 58·6,
   Final distillation showed traces of copper. { Ni 13·8.
2. 0·0022 yielded after distillation of zinc a residue 0·0016. { Zn 27·3,
   and ,, ,, ,, copper ,, 0·0002. { Cu 63·6,
   Final distillation showed traces of copper. { Ni 9·1.
3. 0·0052 yielded after distillation of zinc a residue 0·0036. { Zn 30·8,
   Final distillation copper and nickel together. { Cu & Ni 69·2.

Eureka (Cu, 60; Ni, 40).

1. 0·0020 yielded after distillation of copper a residue 0·0006. Cu 70·0.
2. 0·0016 ,, ,, ,, ,, ,, 0·0006. Cu 62·5.
3. 0·0041 ,, ,, ,, ,, ,, 0·0017. Cu 58·5.

Constantan (Cu, 60; Ni, 40).

0·0058 yielded after distillation of copper a residue 0·0022. Cu 62·1.

Bronze (Cu, 95; Sn, 4; Zn, 1).

1. 0·0268 yielded after distillation of zinc a residue 0·0264. Zn 1·49.
2. 0·0140 ,, ,, ,, ,, ,, 0·0138. Zn 1·43.
3. 0·0063 ,, ,, ,, ,, ,, 0·0062. Zn 1·59.

Antimony–Lead (Pb, 50; Sb, 50).

1. 0·0026 yielded after distillation of antimony a residue 0·0012. Sb 53·8.
2. 0·0129 ,, ,, ,, ,, ,, 0·0070. Sb 45·7.

Impure Cadmium (containing aluminium).

1. 0·0190 yielded after distillation of cadmium an oxidised residue 0·0003. Al_2O_3 1·58.
2. 0·07415 ,, ,, ,, ,, ,, ,, 0·00175. Al_2O_3 2·36.
3. 0·0555 ,, ,, ,, ,, ,, ,, 0·00117. Al_2O_3 2·11.
4. 0·2254 ,, ,, ,, ,, ,, ,, 0·0036. Al_2O_3 1·60.
5. 0·0651 ,, ,, ,, ,, ,, ,, 0·0013. Al_2O_3 2·0.

The residue remained as a lightly coherent film of alumina. The percentage of aluminium, therefore, is about half the mean residue, that is, about 1 per cent.

Aluminium–Zinc.

1. 0·0093 yielded after distillation of zinc a residue 0·0019. Al 20·43.
2. 0·0032 ,, ,, ,, ,, ,, 0·0006. Al 18·75.
3. 0·0097 ,, ,, ,, ,, ,, 0·0022. Al 22·68.
4. 0·0102 ,, ,, ,, ,, ,, 0·0020. Al 19·61.

Bismuth, Zinc (Bi, 50; Zn, 50).

1. 0·0022	yielded after distillation of zinc a residue	0·0012.	Bi 54·5.
2. 0·0036	,, ,, ,, ,, ,,	0·0016.	Bi 44·5.
0·0022	,, ,, ,, ,, ,,	0·0010.	Bi 45·5.

Ferro-zinc (Zn, 95; Fe, 5).

0·0071	yielded after distillation of zinc a residue	0·0004.	Zn 94·4.
0·0150	,, ,, ,, ,, ,,	0·0011.	Zn 92·7.

Ferro-manganese (Mn. 90; Fe, 10).

A rough approximation to the proportions of the constituents present in the more refractory alloys may be made by an inspection of their sublimates. The separation of iron and manganese which occurs by the removal of the manganese as the buff oxide is tedious when the manganese is present in large proportions. A anganese containing about 10 per cent. of iron was treated in e furnace. A free evolution of manganese oxide at first takes ace, becoming less copious in succeeding distillations until a ght residue is left, consisting chiefly of iron. The following sults were obtained:

1. 0·0025	gave after distillation of manganese a residue	0·0005.	Mn 80·0.
2. 0·0033	,, ,, ,, ,, ,,	0·0004.	Mn 87·9.
3. 0·0036	,, ,, ,, ,, ,,	0·0007.	Mn 80·6.
4. 0·0070	,, ,, ,, ,, ,,	0·0007.	Mn 90·0.
5. 0·0081	,, ,, ,, ,, ,,	0·00095.	Mn 88·3.
6. 0·0027	,, ,, ,, ,, ,,	0·0002.	Mn 92·6.
7. 0·0019	,, ,, ,, ,, ,,	0·0004.	Mn 78·9.

The difficulty of this separation is further increased by the milarity in the deposits of small quantities of the oxides of iron id manganese.

As illustrative of the delicacy of detection of certain elements, may be pointed out that the zinc present in 0·0005 gram of ronze coinage is quite easily visible when distilled on to glass, e actual quantity being only 5×10^{-6} gram. Previous experiments have shown that lead and arsenic can be detected in uantities of the same order of magnitude (Fletcher, *Sci. Proc. Roy. Dubl. Soc.*, 1913, **13**, 460).

The following are particulars of experiments showing analyses f residue and sublimate:

Brass (Cu, 65·23; Zn, 33·95; Fe, 0·82; Sn, trace).

Owing to the difficulties arising in analysing by this method, quantities suitable for gravimetric estimation which would necessitate larger carbons and disproportionately heavier currents, the residues from several separate analyses were examined together.

Conditions of Experiment.—The temperature was raised until distillation appeared nearly complete, when the current was cut off for examination of the sublimate. The residue was then re-heated until the sublimate showed traces of copper. Approximate total time of heating, one to two minutes in several periods of some seconds. Approximate temperature, 900°, rising in successive sublimations to about 1500° for the last traces of zinc. Percentages of residual copper obtained: 66·44, 65·16, 66·08, 64·[illegible], 67·60; mean, 65·99.

In the tables the first column gives the composition obtained from two previous, and sometimes independent wet analyses. The second column gives the total weight of residues analysed, with the quantities of the original constituents contained therein. The last two columns show the analyses of residue and sublimate respectively, calculated to show the percentages on the original alloy. The portion "unaccounted," obtained by difference, does not involve a large actual error, and probably represents a deficiency in the analysis, in which case the analyses of residue and sublimate may be regarded throughout as satisfactorily complementary, and in very fair accordance with the results obtained.

Wet Analyses.

Initial brass.		Residue 0·2505.	Per cent. on original weight.	Sublimate per cent. on original weight.
Cu	65·23	0·2283	60·00	1·79
Zn	33·95	trace	—	32·23 [illegible]
Fe	0·82	,,	—	none
Sn	trace	,,	—	,,
Unaccounted		0·0222	5·08	,,

The result should show from this a net excess of less than 3·29 per cent. It shows, in fact, a deficiency of only 0·06 on the wet analysis.

Brass * (Cu, 64·32; Zn, 35·68; Ni, 2·85; Fe, 1·76).

Conditions of Experiment.—Six separate quantities of average weight 0·08704 were treated. They were raised to the required temperature range (about 1200°) on a carbon rod 7 mm. in diameter, filed to the core in the centre, by a current of 25 amperes. The time of heating was in all one to two minutes in periods of about twenty seconds, with intermediate cooling for examination. The percentages of residue in each case were: 65·69, 65·58, 66·[illegible], 68·70, 68·14, 68·35; mean, 67·18. This average compares favourably with the previous mean result on three analyses of 68·37.

* Same specimen as previously examined.

Wet Analyses.

Initial brass.		Residue 0·3512.	Per cent. on original weight.	Sublimate per cent. on original weight.
Cu	64·32	0·3073	58·84	2·42
Zn	35·68	none	—	32·54 (diff.)
Ni	2·85	0·0100	1·91	none
Fe	1·76	0·0062	1·19	0·17
Unaccounted		0·0277	5·31	—

The unaccounted portion is partly explicable on the retention of carbon in the residue (apparent on subsequent solution) and the slight partial oxidation of the surface film of the residual pellets. The combined effect of these errors is very small, amounting on several close experiments with similar quantities of copper to only 0·5 per cent., the remaining deficiency of about 4·8 per cent. being probably accounted for in the loss on analysis. An examination of these numbers shows that the analysis should yield an excess percentage of the refractory constituents of 5·31, and a counteracting deficiency of 2·59, due to the volatilisation of the copper and iron found in the sublimate. This leaves a net result of 2·72 per cent. of excess. There is, in fact, a deficiency of 1·75 per cent. in the estimation of the residual constituents. The errors of excess and deficiency in practice nearly balance one another, and in the previous experiments already cited the error amounted only to 0·58 per cent. The figures are satisfactorily close in view of the small quantities dealt with, and seem to indicate the possibility of a brass analysis by this method to within 1 or 2 per cent.

Tin Lead Alloy (Sn, 48·94; Pb, 51·06).

Particulars of Experiment.—This alloy can only be analysed under conditions allowing of free access of air, as the separation depends on the oxidation of the lead and the removal of its oxide. This is best done by using small quantities. Five portions, amounting in all to 0·2606 gram, were analysed. Each portion was heated in four or five separate periods of twenty to thirty seconds to a temperature of about 1000°. The evolution of litharge was at first copious, and finally scarce, and mixed with stannic oxide. The results obtained were: tin, 42·31, 40·00, 41·66, 42·86, 41·09; mean, 41·58.

Wet Analyses.

Initial alloy.		Residue 0·10835.	Per cent. on original weight.	Sublimate per cent. composition.
Sn.........	49·40	0·09963	38·23	7·11
Pb...	50·60	trace	—	51·12
Unaccounted		0 00872	3·35	—

The conclusion from these results is that a 50 per cent. alloy

of these metals is not capable of analysis by this method in air to within 8 or 9 per cent. If we assume the unaccounted portion to be mainly due to deficiency of analysis, then in an alloy of these proportions about 7 per cent. of tin passes into the sublimate. The actual deficiency on five experiments was 7·82. The error will be increased or diminished directly according to the proportion of lead.

Tin Lead Alloy (Sn, 82·12; Pb, 17·88).

Conditions of experiment the same as before. Nine separate fractionations were made, using small quantities, and similar difficulties were experienced. The results obtained were: tin, 76·3[illegible], 77·50, 73·53, 75·91, 78·18, 73·47, 79·26, 75·36, 78·69; mean, 76·4[illegible]. A wet analysis yielded the following results:

Wet Analyses.

Initial alloy.		Residue per cent. on original.	Sublimate per cent. on original.
Sn	82·12	76·24	4·3
Pb	17·88	0·3	18·3

It appears from these numbers that with lead–tin alloys in which the lead is below 20 per cent. the separation can be effected by distillation in air to within about 6 per cent. The actual deficiency on nine fractionations was 5·65, and the analysis showed 4·3 per cent. of tin in the sublimate.

Aluminium Cadmium (Al, 86·67; Cd, 13·33).

Conditions of Experiment.—The filing is heated slowly to about 1000° for some fifteen to thirty seconds, when the cadmium distils off freely. Although the separation is in most cases fairly complete, the tendency of this alloy to decrepitate during the evolution of cadmium prevents an accurately quantitative analysis. About 2 centigrams were used for each fractionation, and the following results were obtained: aluminium, 79·5, 85·7, 88·5, 86·3, 78·3, 86·5, 82·4, 84·6, 86·4; mean, 84·24. A number of deficient results are excluded.

Wet Analyses.

Initial alloy.		Residue 0·1379.	Per cent. on original weight.	Sublimate per cent. on original weight.
Al..............	86·67	0·1302	80·0	0·2
Cd	13·33	0·0077	4·5	16·9

The wet analyses were made on all the residues, among which were particles, which owing to decrepitation had been insufficiently heated, and yielded abnormal results. The amount of cadmium retained is therefore usually below the 4·5 per cent. above.

Mineral Analysis.

Perhaps the most useful possibility for the micro-furnace lies in its application to the rapid determination of minerals of doubtful purity, in which field of work its value is enhanced on account of the small quantities necessary for an analysis, and the ease and rapidity with which such analysis is carried out. An inspection of the foregoing deposits resulting from the distillation of the constituents of a mineral from carbon at high temperatures is quite fairly sufficient for its determination without a gravimetric separation, and with some practice such analyses can be made with a fair amount of accuracy owing to the concentric arrangement of the deposits according to their relative volatilities. The following results are given in illustration of its application in this respect. The analyses occupied in each case a few minutes only.

Sylvanite.

0·00365 yielded after distillation 0·0016.	Te 56·1.
A second distillation yielded chiefly silver 0·00095.	Ag 17·8.
The residue separated mechanically into gold	Au 21·9.
and some impurity resembling silica.	Impurity 4·2.

There is a tendency to a mechanical separation of silver from the gold in the residue from the distillation of the tellurium:

0·00765 yielded after distillation 0·00365.	Te 52·3.
	Au and Ag 47·7.

Psilomelane.

0·0024 gave	after	distillation	a residue	of	Mn 0·0018.	Mn 75.
0·0041	,,	,,	,,	,,	Mn 0·0029.	Mn 71.
0·0010	,,	,,	,,	,,	Mn 0·00075.	Mn 75.
0·0045	,,	,,	,,	,,	Mn 0·00325.	Mn 72.
0·0031	,,	,,	,,	,,	Mn 0·0023.	Mn 74.
0·0087	,,	,,	,,	,,	Mn 0·0065.	Mn 75.

The above rough approximations to the percentages of the minerals dealt with, together with the characteristic appearances of the deposits produced by each mineral, would be of very great assistance in identifying the mineral.

Sufficient has been said to indicate both the value and the limitations of the method. The possibility of a separation is in most cases bound up with the relative volatility of the metal or its compound formed under the influence of the particular atmosphere in which the distillation is made. As yet only a few alloys have been examined, and those in air, and it is hoped that the method may find extension both in its application to the qualitative analysis and determination of minerals by their characteristic sublimates,

and in the more accurate quantitative separation of metals under the influence of atmospheres other than air.

I am indebted to Professor G. T. Morgan and to Dr. J. H. Pollok for their continued interest in the course of these experiments, and to Professor Grenville A. J. Cole for the mineral specimens examined.

CHEMICAL LABORATORY,
ROYAL COLLEGE OF SCIENCE FOR IRELAND,
DUBLIN.

CCXIII.—*Resolution of α-Anilinostearic Acid.*

By HENRY RONDEL LE SUEUR.

THE resolution of α-anilinostearic acid was undertaken in order to obtain an optically active amphoteric substance, which was required for an investigation with which the author has been engaged for some time. It was essential that the active substance should be not only feebly amphoteric, but also insoluble in water and in organic solvents generally, and both of these conditions are fulfilled by α-anilinostearic acid.

At the outset the fractional crystallisation of the quinine salt of the anilinostearic acid was carried out, but although the salt was recrystallised ten times, the free acid obtained from it had very little optical activity. It was then found that dissociation of the quinine salt took place during the recrystallisation, with the result that the solid which separated out from the solution on cooling consisted largely of the free acid. Thus, in one experiment, 7·5 grams of what was supposed to be the true quinine salt gave 6·5 grams of free acid after removal of the quinine, and this is far in excess of what should have been obtained even if the quinine had acted as a diacid base. To overcome this difficulty, due to dissociation, the alkaloidal salt was recrystallised from solutions containing a large excess of the free alkaloid, but although a better result was obtained, nevertheless a complete resolution was not effected by this method. Thus, in one experiment, 45 grams of anilinostearic acid and 90 grams of quinine were dissolved in one litre of hot alcohol, and the solution kept at 5° for several days, at the end of which time 78 grams of the quinine salt were obtained. These were recrystallised from alcohol containing an amount of quinine equal to half the weight of the

amine salt, and after repeating this process seven times, a dextro-acid was obtained, having an optical activity of $[\alpha]_D + 11·5°$ in pyridine. This result was not regarded as satisfactory, and attempts were made to effect the resolution by means of morphine and cinchonine, but with no better results, and the idea of using alkaloids had to be abandoned.

Experiments were then made with *l*-menthylamine as a base, and it was found that this substance forms a well-crystallised and stable salt with α-anilinostearic acid, and by means of this base the desired resolution was effected. For this purpose 35 grams of α-anilinostearic acid and 14 grams of *l*-menthylamine were dissolved in a mixture of 250 c.c. of alcohol and 30 c.c. of ethyl acetate, and the solution kept in a cold place. The menthylamine salt gradually separated out in aggregates of long, flat needles, and at the end of eight days these were collected (filtrate *A*), and after drying weighed 17 grams. These were then recrystallised once from a mixture of alcohol and ethyl acetate, and then from alcohol alone until the activity of the acid, which was dextrorotatory, was not increased by further recrystallisation. That the resolution was complete was further proved by recrystallising the acid itself, when it was found that both its melting point and rotatory power were constant.

Pyridine was used for determining the rotation of the acid, as it is quite insoluble in water, and its solubility in the ordinary organic solvents in the cold is far too small to admit of their being used for this purpose. The values thus obtained are consequently those of the pyridine salt in solution in pyridine:

0·4648 of acid, dissolved in pyridine, made up to 15 c.c., and examined at 19° in a 2-dcm. tube, gave $\alpha_D^{19} + 2·15°$, whence $[\alpha]_D^{19} + 34·7°$.

The *d*-anilinostearic acid is sufficiently soluble in alcohol at 40° for its rotation to be determined in this liquid at this temperature, and for the determination under these conditions the author is indebted to Mr. G. W. Clough, who obtained the following result:

$l = 4$; $c = 0·6037$; $\alpha_D^{40} + 0·45°$, whence $[\alpha]_D^{40} + 18·6°$ in solution in alcohol.

d-α-Anilinostearic acid, $C_{16}H_{33}·CH(NHPh)·CO_2H$, is insoluble in light petroleum, chloroform, or benzene in the cold, sparingly so in cold ether, ethyl acetate, or acetone, and moderately soluble in hot alcohol, from which it crystallises on cooling in aggregates of flat needles, melting at 129–130° (Found, N = 3·85. $C_{24}H_{41}O_2N$ requires N = 3·73 per cent.). The melting point of inactive anilinostearic acid is 141—142° (T., 1910, **97**, 2435).

The *l-menthylamine* salt of *d*-anilinostearic acid is readily soluble

in ether, chloroform, or benzene, and crystallises from alcohol in aggregates of long needles, flat needles, melting at 61—63°:

0·2308 gave 10·4 c.c. N_2 (moist) at 17° and 765 mm. N=5·26.

$C_{24}H_{41}O_2N,C_{10}H_{21}N$ requires N=5·28 per cent.

The filtrate *A* (p. 2109), obtained in the first crystallisation of the menthylamine salt of the inactive anilinostearic acid, was concentrated to 120 c.c., and allowed to remain for some time, when 2·8 grams of solid separated. This was collected, and the filtrate concentrated to 50 c.c., but as no solid separated the solution was poured into dilute sulphuric acid, and the precipitated acid collected, well washed and dried. After two recrystallisations from alcohol its rotation in pyridine was $[\alpha]_D^{20} -18°$. The acid was recrystallised three times more from alcohol, then again converted into its menthylamine salt, and this recrystallised from alcohol. Finally, the acid was again liberated from its salt, and after three recrystallisations from alcohol melted at 128—129°, and a determination of its rotation in pyridine gave the following result:

$l=2$, $c=2·38$; $\alpha_D^{19} -1·44°$; whence $[\alpha]_D^{19} -30·2°$ in solution in pyridine

l-α-*Anilinostearic acid* crystallises from alcohol in aggregates of flat needles, and its solubility in various solvents corresponds with that of its *d*-isomeride.

CHEMICAL LABORATORY,
ST. THOMAS'S HOSPITAL,
LONDON, S.E.

CCXXIV.—*Bismuthinitrites.*

By WALTER CRAVEN BALL and HAROLD HELLING ABRAM.

IN previous communications (T., 1905, **87**, 761; 1909, **95**, 2126; 1910, **97**, 1408) one of the authors of the present paper has described several compounds of bismuth nitrite with the alkaline nitrites. These compounds were chiefly remarkable as affording a method for the gravimetric estimation of sodium, and for its separation from potassium, owing to the insolubility of cæsium sodium bismuthinitrite and the non-formation of the corresponding potassium salt (T., 1910, **97**, 1408). As it is unusual to find such sharp differences in the behaviour of sodium and potassium salts, the present authors have investigated all the salts of this series which they have been able to obtain, in order to discover, if possible, other facts bearing on this difference in behaviour. The salts which have been obtained all fall into two groups, of which

the general formulæ are respectively $X_3Bi(NO_2)_6$ and $X_2YBi(NO_2)_6$. In these formulæ X represents any of the metals ammonium, potassium, rubidium, cæsium, and thallium, whilst Y stands for either lithium, sodium, or silver.

There are thus possible five compounds of the $X_3Bi(NO_2)_6$ series, the simple bismuthinitrites, and of these, four have been obtained, the attempts to obtain the ammonium salt having been so far unsuccessful owing to the great instability of concentrated solutions of ammonium nitrite in the presence of acid.

Although the ammonium salt has not been obtained, bismuthinitrites of several organic nitrogenous bases, such as cocaine and brucine, can easily be prepared.

Of the mixed bismuthinitrites of the general type $X_2YBi(NO_2)_6$, fifteen are possible; for each of the metals X might exist together in a compound with any of the three metals represented by Y. These compounds have all been obtained.

Although many attempts have been made to prepare compounds, in the solid state, containing two metals of the X series together, or two metals of the Y series together, they have been entirely unsuccessful. The same remark applies to all the attempts the authors have made to obtain compounds in the solid condition, containing two atoms of a Y series metal with one atom of an element represented by X, or to prepare compounds having the formula $Y_3Bi(NO_2)_6$. The simple bismuthinitrites of sodium and of lithium probably exist in solution, for deep orange-coloured liquids result when bismuth nitrate is added to solutions of the nitrites of these metals, just as happens in the case of potassium nitrite or of rubidium nitrite. Whereas, however, the bismuthinitrites of the two latter metals can be precipitated from their solutions, this cannot be done with lithium or sodium.

The apparent impossibility of preparing mixed bismuthinitrites containing only metals of the X series, or of the Y series, is well shown by adding cæsium nitrate to separate solutions of the nitrites of sodium and of potassium each containing bismuth. With the sodium solution there occurs an immediate precipitate of the mixed salt, sodium cæsium bismuthinitrite, even when traces only of cæsium salt are added. With the potassium solution there is no apparent change until a large quantity of cæsium has been added, when a precipitate of the simple cæsium bismuthinitrite gradually settles. Again, silver nitrate, the nitrate of an element of the Y series, when added to a solution of sodium nitrite containing bismuth, produces no deposition of a mixed compound containing two elements of the Y series, but on the addition of a potassium solution, or of a solution of any of the metals of the X series, there is at once a precipitation of the mixed X–Ag salt.

This difference in behaviour between sodium and potassium, which, as above-mentioned, is sufficiently pronounced to form a method of separating them, is now to some extent explained; i.e. potassium, being a metal of the X series, will not form a mixed bismuthinitrite with cæsium, also a metal of this series, whereas sodium, belonging to the Y series, will do so. As the cæsium sodium salt is a very insoluble one, the metal can in this way be separated from potassium, collected, and weighed.*

In a similar manner, cæsium and rubidium may be separated from potassium,† for on adding a mixture of salts of the three metals to a concentrated solution of sodium nitrite containing bismuth, the mixed bismuthinitrites of sodium with cæsium, and of sodium with rubidium, will precipitate, being only very sparingly soluble, whilst the very soluble potassium sodium salt remains in solution. It seems, then, necessary, in order that a mixed bismuthinitrite should be capable of existence, that it should contain a metal of the isomorphous series, (NH_4), K, Rb, Cs, Tl, together with one belonging to the isomorphous series, Li, Na, Ag, the metal of the former series being present in the greater atomic proportion.

A further series of five compounds exists, containing nickel in addition to a metal of the X series. These compounds are precipitated when a nickel salt is added to the solution of a nitrite of

* Incidentally, this explains another fact noticed in studying the estimation of sodium as sodium cæsium bismuthinitrite. The reagent used contained 30 grams of potassium nitrite, 3 grams of bismuth nitrate, and about 1·5 grams of cæsium nitrate per 100 c.c., and produced a yellow precipitate of sodium cæsium bismuthinitrite on the addition of traces of a sodium salt. When a reagent containing less potassium nitrite was made up, it was noticed that part of the cæsium would gradually deposit as cæsium bismuthinitrite, more being thus precipitated the lower the concentration of the potassium nitrite. Conversely, when the reagent contained more than 30 grams of potassium nitrite per 100 c.c., it could hold more cæsium salt without deposition of cæsium bismuthinitrite. There would appear to be an equilibrium between the amounts formed of the very soluble potassium bismuthinitrite and of the relatively insoluble cæsium bismuthinitrite, the concentration of the latter, when high concentrations of potassium nitrite were used, failing to reach the value necessary for precipitation. These facts seem to render unlikely the existence, even in solution, of a potassium cæsium bismuthinitrite.

† Cæsium may also be separated from rubidium by taking advantage of the greater insolubility of the cæsium sodium bismuthinitrite. Thus, if a mixture of cæsium and rubidium nitrates is added to a concentrated solution of potassium nitrite containing bismuth, and then a sodium salt gradually, the cæsium sodium bismuthinitrite will precipitate with a very small concentration of sodium, whilst the rubidium will remain in solution until a much greater concentration of sodium is attained. One of the authors has used this method satisfactorily for separating cæsium from an impure rubidium chloride obtained in the extraction of lithium. The separation has not been investigated quantitatively, and some rubidium remains in solution.

of these metals, in presence of bismuth. The Y metals do not appear to form any mixed compounds with nickel.

The bismuthinitrites resemble the cobaltinitrites closely in form, colour, and solubility in many cases; thus silver produces no precipitate with lithium or sodium cobaltinitrite, nor with sodium or lithium solutions containing bismuth (sodium and lithium bismuthinitrites), but on the addition of a salt of a metal of the X series the corresponding X–Ag cobaltinitrite or bismuthinitrite is precipitated as a yellow or red, crystalline powder.

In preparing the bismuthinitrites, chlorides should be absent, or present in only very small amount; otherwise bismuth oxychloride will precipitate.

As the bismuthinitrites are all hydrolysed by water, in most cases rapidly, it is impossible, as a rule, to wash them. They are generally prepared by precipitation from a strong solution of a nitrite, and it is, in consequence, difficult to remove all traces of mother-liquor from the preparations. The most that can be done is to remove the mother liquor as completely as possible by the aid of the pump, and then to press the crystals on porous plates. The nearly dry crystals are then kept for some hours, under pressure, between sheets of filter paper. Fortunately, the salts are highly crystalline, which renders it easier to remove mother liquor, but the difficulty of completely effecting this removal frequently shows itself slightly in the analyses; thus the thallous sodium salt, which is precipitated on adding a thallous salt to a strong solution of sodium nitrite containing bismuth, shows a rather too high percentage of sodium. This effect on the analytical results is hardly evident in the case of the less soluble bismuthinitrites, such as the silver salts, for these can be precipitated from a less concentrated mother liquor, but is chiefly seen in those which are the most soluble.

The proportions of the different salts used in the preparation of the various bismuthinitrites may, as a rule, be considerably varied, and those given are simply the amounts which the authors have found to yield good results. In a few cases, such as that of the potassium sodium bismuthinitrite, the salt is formed with difficulty, and the proportions given cannot be much departed from. Frequently the method of preparation may be reversed; thus potassium lithium bismuthinitrite may be made either by adding lithium nitrate to a solution of potassium nitrite containing bismuth, or by adding potassium nitrate to the corresponding lithium nitrite solution.

The nitrites used should be as pure and as free from alkali as possible. For convenience, the description of the various bismuthinitrites is divided into three parts. Part I describes the simple

bismuthinitrites; Part II the mixed salts; and Part III the salts containing nickel.

Part I.

The Simple Bismuthinitrites.

These salts form yellow or orange, hexagonal plates. They are less stable and more soluble, on the whole, than the mixed salts, from which they differ also in crystalline form. The potassium and rubidium salts are very unstable, as indeed are all the bismuthinitrites that contain water. In the case of cæsium, which is the most electropositive of the metals, the formula of the salt is $Cs_3Bi(NO_2)_6.Bi(NO_2)_3$, and in the case of thallium, which is the least electropositive of the metals concerned, it is

$$Tl_3Bi(NO_2)_6,TlNO_2,H_2O.$$

It is a curious fact that the more strongly electropositive cæsium should be able to combine with more bismuth nitrite, whereas the much less electropositive thallium should need an extra molecule of thallium nitrite in order to form its salt.

The potassium and rubidium salts have the normal formulæ $K_3Bi(NO_2)_6,H_2O$ and $Rb_3Bi(NO_2)_6,2H_2O$, but it is possible that other hydrates of the two salts exist.

Potassium Bismuthinitrite, $K_3Bi(NO_2)_6,H_2O$.

The properties and composition of this salt were given in a former paper. It was previously prepared by passing nitrous fumes into a suspension of bismuth hydroxide in concentrated aqueous potassium nitrite, but can also be obtained by adding bismuth nitrate to a very concentrated aqueous solution of this salt.

The solution of bismuth nitrate used throughout the work described in this paper was made by warming 50 grams of crystalline bismuth nitrate with 10 c.c. of fuming nitric acid and a little water. After dissolution of the salt, the liquid was made up to 100 c.c. with water.

When some of this bismuth solution is added to four times its volume of an 80 per cent. solution of potassium nitrite, potassium bismuthinitrite is precipitated in fine, golden plates. Access of air must be avoided as much as possible, and the solution must not be cooled, for although this gives a larger yield of the salt, it leads to contamination with potassium nitrate. The salt should be collected by the aid of the pump, pressed on a porous plate, and dried finally by pressure between sheets of filter-paper.

It crystallises in large, golden-yellow or orange plates, is unstable.

and cannot be kept, at the ordinary temperature, for more than a few days. Its properties and full analyses were given in the former paper.

Rubidium Bismuthinitrite, $Rb_3Bi(NO_2)_6,2H_2O$.

This salt can best be prepared by adding bismuth nitrate solution to a concentrated solution of rubidium nitrite (see p. 2131). On adding 3 or 4 c.c. of the bismuth solution to 20 or 30 c.c. of 50 per cent. rubidium nitrite solution, the salt is rapidly precipitated. It is collected and dried as for the potassium salt. It is very unstable, even more so than the potassium salt, probably because it contains two molecules of water. Other hydrates possibly exist.

It forms orange-yellow plates, which on keeping become white, with evolution of oxides of nitrogen. It is considerably less soluble than the potassium salt.

Found: Rb = 33·56; Bi = 26·74; NO_2 = 35·44, 35·75; H_2O (by difference) = 4·26.

$Rb_3Bi(NO_2)_6,2H_2O$ requires Rb = 33·01; Bi = 26·79; NO_2 = 35·55; H_2O = 4·65 per cent.

Caesium Bismuthinitrite, $Cs_3Bi(NO_2)_6,Bi(NO_2)_3$.

This substance can be obtained by adding bismuth nitrate solution to cæsium nitrite solution (prepared from cæsium sulphate and barium nitrite, p. 2130). It is much less soluble than the two preceding salts, so that less concentrated solutions may be used in its preparation.

It is obtained by adding one or two drops of nitric acid, then gradually 2 or 3 c.c. of bismuth nitrate solution to 20 c.c. of a 5 per cent. solution of cæsium nitrite, shaking continually. A voluminous, yellow, crystalline precipitate is formed at once, which is collected after a few minutes, and dried as for the previous salts. It may also be prepared by adding cæsium nitrate to a solution of potassium nitrite containing bismuth. To prepare it in this manner, 20 grams of the nitrite (as free from sodium as possible) are dissolved in about 40 c.c. of water; then about 7 c.c. of the bismuth nitrate solution are added, together with enough nitric acid to dissolve any precipitate (due to free alkali in the potassium nitrite) which may be produced. To the clear liquid 5 c.c. of a 10 per cent. solution of cæsium nitrate are added, and it is kept in a closed vessel (provided with a Bunsen valve for the escape of oxides of nitrogen) for several hours. Should any yellow precipitate be produced (cæsium sodium bismuthinitrite, due to traces of sodium in the reagents used) it is collected, and about 20 c.c. more of the

cæsium solution are added. The precipitate of cæsium bismuthinitrite should be collected after several hours' keeping.

It consists of golden to orange, hexagonal plates, closely resembling lead iodide. Contrary to expectation, the salt was found to give results on analysis agreeing with the formula $Cs_3Bi(NO_2)_6,Bi(NO_2)_3$, the percentages of cæsium and of bismuth being about the same, and corresponding therefore with the atomic ratio 3Cs : 2Bi.

Found: Cs = 33·43, 32·8; Bi = 33·80, 33·4; NO_2 = 33·0.

$Cs_3Bi(NO_2)_6,Bi(NO_2)_3$ requires Cs = 32·44; Bi = 33·87; NO_2 = 33·7 per cent.

On account of the flaky nature of the crystals it is difficult to free this salt entirely from its mother liquor.

Thallium Bismuthinitrite, $Tl_3Bi(NO_2)_6.TlNO_2.H_2O$.

For this preparation it is necessary to use a solution of thallous nitrite (the preparation of this salt is described in the following paper, p. 2131) containing 20 per cent. or more of the salt. To 50 c.c. of this orange-coloured solution (the solid thallous nitrite is red) are added a few drops of acetic acid,* and then gradually 2 to 3 c.c. of the bismuth solution. A golden-yellow, crystalline precipitate is formed, which must be collected and dried as quickly as possible. Should the substance tend to decompose and turn white during its preparation, this is due to deficiency of nitrite in the solution ($TlNO_2$ contains less than one-fifth of its weight of NO_2), and may be remedied by the addition of a little 50 per cent. potassium nitrite solution; too much of this salt will cause the precipitate to redissolve.

The salt forms fine, golden-yellow, hexagonal plates, which have a high specific gravity. It is unstable, gradually becoming white.

Found: Tl = 59·8; Bi = 15·2.

$Tl_3Bi(NO_2)_6,TlNO_2,H_2O$ requires Tl = 59·8; Bi = 15·25 per cent.

The numbers found for the bismuth and thallium agree very accurately therefore with the proportions required by the formula suggested. The same would, however, apply to the formula $Tl_3Bi(NO_2)_6,TlNO_3$ almost equally well; for in it the ratio of bismuth to thallium is the same, and the molecular weights are nearly the same. It is clear that a direct determination of the amount of nitrite present would settle which of the formulæ is correct, but, unfortunately, we were unable to devise a method for the estimation of nitrite in the presence of thallium, which should at the same time distinguish between nitrous and nitric nitrogen.

* Acetic acid rather than nitric; for thallium acetate is much more soluble than the nitrate, and therefore less likely to contaminate the precipitated compound.

The method employed throughout this work for the estimation of nitrogen was to oxidise the nitrite to nitrate by means of an excess of acid permanganate at 0°, titrating the excess of permanganate with a ferrous salt. When a thallium salt was present, this was also oxidised to the thallic state, but always incompletely. Experiments made with thallous sulphate showed that at 0°, and under the conditions used, very nearly two-thirds of the thallium was oxidised to the thallic state (or, alternatively, that the whole of the thallium was oxidised to an intermediate stage of oxidation; we have not yet had an opportunity to test the point further). If, however, both thallium and a nitrite were present, the oxidation of the thallium was more complete than if thallium alone had been present.

Thus, although it is impossible, in this way, to estimate exactly the amount of nitrite in those bismuthinitrites which contain thallium, yet by finding the amount of oxygen absorbed from permanganate it is possible to estimate the nitrite approximately.

In the case of thallium bismuthinitrite, for example, if the formula were $Tl_3Bi(NO_2)_6,TlNO_3$, the percentage amount of oxygen absorbed would be 11·75, on the assumption, never quite realised, that the thallium is completely oxidised to the thallic state. The percentage found, 12·3, was greater than this, so that this formula must obviously be incorrect. The alternative formula,

$$Tl_3Bi(NO_2)_6,TlNO_2,H_2O,$$

would, on the assumption of complete oxidation of the thallium, require 12·90 per cent. of absorbed oxygen. The amount of oxygen absorbed, representing that required for the complete oxidation of the nitrite plus that required for the partial oxidation of the thallium, therefore confirms the formula $Tl_3Bi(NO_2)_6,TlNO_2,H_2O$.

In the case also of the other bismuthinitrites containing thallium, the amount of oxygen absorbed is given, instead of the amount of nitrite.

PART II.

Mixed Bismuthinitrites.

These salts are, in general, less soluble and more stable than the simple bismuthinitrites. In consequence of their less solubility, they are more easily prepared. In crystalline form they differ from the plate-shaped crystals of the simple salts, forming crystals which appear to be octahedral. They vary in colour from the pale yellow of the cæsium silver salt to the red of the thallium silver compound.

With the exception of those containing water of crystallisation, such as the lithium ammonium salt, they are relatively stable, and

can be kept unaltered for months. Some of them, such as the cæsium sodium salt, remain unaltered at 100°. They are, however, very liable to rapid decomposition under certain conditions; for example, a large number of specimens of the various compounds which had been kept unaltered for weeks, in a store desiccator, were found to have all suffered decomposition, more or less complete, shortly after the introduction into the store vessel of a specimen of the potassium nickel salt. The decomposition appeared to be due to the slow liberation of oxides of nitrogen from the very unstable potassium nickel salt. There have been, however, other cases of the sudden decomposition of specimens that had remained for a long time unaltered, for which there were no obvious causes. On account of this instability, specimens of some of the salts were kept for some days in contact with a closed tube containing 5 milligrams of radium bromide, but there was no evidence of decomposition, nor was any phosphorescence produced. Short exposures to Röntgen radiation also produced no perceptible effect. Light acted very slowly on the silver salts, producing a gradual blackening.

For convenience, the mixed bismuthinitrites are divided into three groups: Group A containing those salts in which the metal represented by Y in the general formula $X_2YBi(NO_2)_6$ is lithium; group B, those in which Y is silver; group C, those in which Y is sodium.

Group A. Bismuthinitrites containing Lithium.

Ammonium Lithium Bismuthinitrite, $(NH_4)_2LiBi(NO_2)_6,H_2O$.

To about 16 c.c. of a 50 per cent. solution of lithium nitrite (the preparation of this salt is described in the following paper, p. 2133) are added 4 c.c. of the bismuth nitrate solution. The mixture is cooled to 0°, and about 3 grams of ammonium nitrate in 10 c.c. of water are added. After a few minutes, during which time the containing vessel is surrounded with ice, the yellow, crystalline precipitate is collected, dried on a porous plate, and then by pressure between sheets of filter-paper, as previously described.

The salt consists of fine, bright yellow crystals, probably octahedra. It is unstable, and cannot be kept at the ordinary temperature for more than a few days. Water hydrolyses it readily.

Found: $NH_4=6{\cdot}70$; $Li=1{\cdot}23$; $Bi=38{\cdot}4$; $NO_2=50{\cdot}1$; H_2O (by difference) $=3{\cdot}57$.

$(NH_4)_2LiBi(NO_2)_6,H_2O$ requires $NH_4=6{\cdot}62$; $Li=1{\cdot}27$; $Bi=38{\cdot}2$; $NO_2=50{\cdot}6$; $H_2O=3{\cdot}31$ per cent.

Potassium Lithium Bismuthinitrite, $K_2LiBi(NO_2)_6$.

To about 50 c.c. of a 50 per cent. solution of potassium nitrite are added between 5 and 10 c.c. of the bismuth nitrate solution, and 3 or 4 grams of a soluble lithium salt, such as the nitrate or acetate, dissolved in about 20 c.c. of water (as previously mentioned, the chloride must not be used, as it would cause bismuth oxychloride to precipitate). A yellow precipitate of the salt rapidly settles, partly on the walls of the containing vessel, and after an hour or more this is collected and dried, as in the case of the salts previously described.

The preparation may be reversed by adding the solution of a potassium salt to a solution of lithium nitrite containing bismuth.

The salt forms bright yellow, apparently octahedral crystals, resembling the ammonium lithium compound, but quite stable. It is easily hydrolysed by water. Its specific gravity at 15° is 3·21.

Found: K = 13·97; NO_2 = 48·3.

$K_2LiBi(NO_2)_6$ requires K = 13·74; NO_2 = 48·5 per cent.

Rubidium Lithium Bismuthinitrite, $Rb_2LiBi(NO_2)_6$.

To 20 c.c. of 50 per cent. lithium nitrite solution are added about 10 c.c. of the bismuth nitrate solution, then 2 to 3 grams of rubidium nitrate dissolved in enough water to bring the total volume to about 60 c.c.

The compound is precipitated rapidly, and may be collected after about an hour, and dried as previously described. The preparation may be reversed by adding a soluble lithium salt to a solution of rubidium nitrite to which bismuth nitrate has been added.

The salt forms yellow, apparently octahedral crystals, very similar to the potassium lithium salt in all respects, but less soluble. It is a quite stable compound.

Found: Rb = 26·8; Li = 0·97; NO_2 = 41·34.

$Rb_2LiBi(NO_2)_6$ requires Rb = 25·8; Li = 1·05; NO_2 = 41·71 per cent.

Caesium Lithium Bismuthinitrite, $Cs_2LiBi(NO_2)_6$.

To 20 c.c. of 50 per cent. lithium nitrite solution are added 5 to 10 c.c. of bismuth nitrate solution, then 2 to 3 grams of caesium nitrate in enough water to bring the total volume to about 30 c.c. The yellow precipitate is collected after about an hour, and dried as previously described.

The salt forms yellow crystals resembling those of the rubidium salt, but still less soluble. It is quite stable.

Found: Cs = 35·0; Li = 1·00; NO_2 = 36·6.

$Cs_2LiBi(NO_2)_6$ requires Cs = 35·1; Li = 0·92; NO_2 = 36·5 per cent.

Thallium Lithium Bismuthinitrite, $Tl_2LiBi(NO_2)_6$.

To 40 c.c. of a 25 per cent. solution of lithium nitrite in water about 4 c.c. of the bismuth nitrate solution are added, followed by 20 c.c. of a 10 per cent. solution of thallium nitrate or acetate, the addition being made gradually. The salt is collected after about an hour, and dried as previously described.

The colour of this salt differs considerably from those of the other bismuthinitrites, as it is pale brown. It forms bright crystals, probably octahedral. It is quite stable, and rather insoluble.

Found: Tl = 45·4; Li = 0·84; Bi = 23·04.

$Tl_2LiBi(NO_2)_6$ requires Tl = 45·4; Li = 0·77; Bi = 23·1 per cent.

The percentage amount of oxygen absorbed by the salt from permanganate solution at 0° was 13·8 (see p. 2117); assuming that all the thallium was oxidised to the thallic state, it should be 14·2.

Group B. Bismuthinitrites containing Silver.

These salts crystallise well, and, with the exception of the potassium-silver compound, are stable. In the series ammonium silver, potassium–silver, rubidium-silver, and cæsium-silver the solubility and the depth of colour decrease with increasing molecular weight: the ammonium silver salt is red, and the most soluble of the group, the potassium salt, is red inclining to orange, and less soluble, the rubidium–silver compound is orange and still less soluble, and the cæsium–silver salt is yellow and very insoluble. The thallium–silver salt is also of very low solubility, but is red. The specific gravities of these compounds also increase with increasing molecular weight, and have the following values at 15—16°:

Ammonium silver salt.	Found, 3·05, 3·06.	Mean, 3·055.
Potassium–silver ,,	,, 3·32, 3·34, 3·33.	Mean, 3·33.
Rubidium–silver ,,	,, 3·66, 3·68, 3·67.	Mean, 3·67.
Cæsium silver ,,	,, 3·883, 3·875.	Mean, 3·88.
Thallium–silver ,,	,, 4·860, 4·874.	Mean, 4·87.

Ammonium Silver Bismuthinitrite, $(NH_4)_2AgBi(NO_2)_6$.

This salt can be prepared by adding a solution of silver nitrate to a solution of ammonium nitrite containing bismuth nitrate but as acidified solutions of ammonium nitrite are very unstable it is more convenient to add first bismuth nitrate, and then silver nitrate, to a solution of sodium nitrite in water. This mixture does not yield a precipitate of sodium–silver salt, as both these metals belong to the Y group, as previously explained. On now

adding a solution of ammonium nitrate, a red, crystalline precipitate of the ammonium–silver salt will fall.

To 25 c.c. of a 50 per cent. sodium nitrite solution are added 5 c.c. of the bismuth nitrate solution, then with constant shaking about 10 c.c. of a 10 per cent. solution of silver nitrate. The white precipitate of silver nitrite at first produced will dissolve (silver nitrite being soluble in concentrated solutions of the nitrites of the alkali metals), but there will probably remain a slight permanent precipitate of silver chloride, due to chloride almost always present in the reagents. Should this be the case, it is removed by filtration, and about 2 grams of ammonium nitrate dissolved in a very little water are added. A red, crystalline substance will be precipitated, which must be collected after a few minutes. The liquid should be kept cold throughout, and the filtration accomplished as quickly as possible. The substance is dried, as in the case of the former salts.

The substance forms fine, red crystals, apparently octahedral. It is not particularly insoluble, and the crystals can be obtained fairly large. It is quite stable at the ordinary temperature, specimens having remained unaltered after several months. Water hydrolyses it rapidly. When quite dry it explodes very feebly on being rubbed in a mortar, as also do some of the other bismuthinitrites containing ammonium.

Found: $Ag=17{\cdot}2$; $NH_4=5{\cdot}4$; $NO_2=43{\cdot}7$.

$(NH_4)_2AgBi(NO_2)_6$ requires $Ag=17{\cdot}2$; $NH_4=5{\cdot}75$; $NO_2=43{\cdot}9$ per cent.

Potassium Silver Bismuthinitrite, $K_2AgBi(NO_2)_6$.

To 30 c.c. of 50 per cent. potassium nitrite solution are added about 10 c.c. of the bismuth nitrate solution, then silver nitrate (say, 2 per cent. solution) until all chloride that may be present is precipitated, and the orange-red potassium silver bismuthinitrite begins to fall. The mixture is filtered, and to the filtrate about 1 c.c. more of the silver nitrate solution are added gradually and with constant shaking. The salt is collected, and dried as for the other salts. By using a fairly dilute silver solution the substance is obtained in larger crystals. More concentrated solutions may be used, but in that case the salt will be precipitated in minute crystals.

The salts forms orange-red, apparently octahedral crystals. It resembles the ammonium–silver salt closely, but is less soluble. For some reason, which the authors have, so far, been unable to explain, this salt appears to be less stable than the other mixed silver bismuthinitrites. One would expect it to be much more

stable than the ammonium salt, but the reverse is the case, and the preparations hitherto made, about seven in number, have all gradually decomposed and become white on keeping, whereas preparations of the other mixed silver bismuthinitrites, made at the same time and kept under similar conditions, have remained unaltered.

Found: Ag = 16·2; NO_2 = 41·2.

$K_2AgBi(NO_2)_6$ requires Ag = 16·1; NO_2 = 41·2 per cent.

Rubidium Silver Bismuthinitrite, $Rb_2AgBi(NO_2)_6$.

This salt may be obtained by adding bismuth nitrate, and then silver nitrate, to a solution of rubidium nitrite (the preparation of this salt is described in the following paper, p. 2131), but the use of this salt may be avoided in the following manner. If bismuth nitrate, and then rubidium nitrate, are added to a solution of sodium nitrite, the result is the precipitation of rubidium sodium bismuthinitrite. If, however, silver nitrate be added before the rubidium salt, this precipitate will be replaced by an orange-yellow one of the rubidium-silver salt. The amount of rubidium nitrate must be limited, so that there is always enough silver present to form the rubidium-silver compound, to the exclusion of the more soluble rubidium sodium salt.

To 15 grams of pure sodium nitrite (free from potassium) water is added until the volume of the solution is about 80 c.c. To this are added about 5 c.c. of the bismuth nitrate, then gradually, and with shaking, about 15 c.c. of 10 per cent. silver nitrate solution. Should any silver chloride form, it must be filtered off. Finally, about 1 gram of rubidium nitrate dissolved in about 10 c.c. of water is added. After allowing to remain for a short time, the precipitate is collected and dried as previously described.

The salt forms orange-yellow, probably octahedral crystals. It is only very sparingly soluble, and not very rapidly hydrolysed by water.

Found: Ag = 14·2; Rb = 22·3; NO_2 = 36·2.

$Rb_2AgBi(NO_2)_6$ requires Ag = 14·14; Rb = 22·4; NO_2 = 36·2 per cent.

Caesium Silver Bismuthinitrite, $Cs_2AgBi(NO_2)_6$.

Although this compound is the most insoluble of all the bismuthinitrites, it is one of the most difficult to obtain in the pure state. It cannot be obtained pure by adding bismuth nitrate and silver nitrate to a solution of cæsium nitrite, as when thus prepared it is contaminated with the insoluble cæsium bismuthinitrite. An

attempt was made to prepare it by adding bismuth nitrate and cæsium nitrate to a solution of potassium nitrite, then gradually adding silver nitrate in smaller quantity than would be required to precipitate the whole of the cæsium as cæsium-silver salt. It was thought that this might yield a pure product, the cæsium-silver salt being formed exclusively, as it is much less soluble than the potassium-silver compound. This was not the case, as determinations of the nitrite and of the silver showed that the product contained several parts per cent. of the potassium-silver salt (Found. $NO_2=34\cdot5$; $Cs_2AgBi(NO_2)_6$ requires $NO_2=32\cdot2$ per cent.). Better results may be obtained by effecting the precipitation in a more dilute solution of potassium nitrite, but the most satisfactory method is to use a dilute solution of sodium nitrite, conducting the preparation as in the case of the preceding salt, rubidium-silver bismuthinitrite. Although cæsium-sodium bismuthinitrite is an insoluble salt, the cæsium-silver compound is still less soluble, and precipitates preferentially. The quantities to be used and the method of preparation are exactly as described for the rubidium-silver salt.

Found: $NO_2=32\cdot4$.

$Cs_2AgBi(NO_2)_6$ requires $NO_2=32\cdot2$ per cent.

The salt forms pale yellow, very minute crystals, which are very insoluble, and decomposed only slowly by water. It blackens slowly on exposure to light, but in absence of light appears to be stable.

Thallium Silver Bismuthinitrite, $Tl_2AgBi(NO_2)_6$.

This salt cannot readily be obtained by the addition of bismuth nitrate and silver nitrate to thallium nitrite solution, as thallium bismuthinitrite itself is an insoluble compound. It can, however, easily be prepared in a way exactly similar to that described for the rubidium silver and cæsium-silver salts, as it is very much less soluble than the thallium-sodium salt.

To 15 grams of pure sodium nitrite (free from potassium), water is added until the volume of the solution is about 60 c.c., then 5 c.c. of the bismuth nitrate solution, 15 c.c. of 10 per cent. silver nitrate solution, and a few drops of dilute acetic acid are added. The mixture is filtered, if necessary, to remove traces of silver chloride, and to the clear filtrate 20 c.c. of a 5 per cent. solution of thallium nitrate are gradually added. The red precipitate is collected after a few minutes, and dried as in the previous cases.

The salt forms a red, finely-divided, crystalline powder, which is very insoluble, and only slowly decomposed by water. It appears to be quite stable.

Found: $Ag=10\cdot8$; $Tl=40\cdot4$.

$Tl_2AgBi(NO_2)_6$ requires $Ag=10\cdot8$; $Tl=40\cdot8$ per cent.

Group C. Bismuthinitrites containing Sodium.

These are all bright yellow, crystalline salts, and they differ very much in their solubilities. The ammonium-sodium salt is very soluble, and can only be obtained from concentrated solutions; the potassium salt is extremely soluble, can only be prepared from solutions of definite concentration, and has probably not yet been obtained in a pure state; the rubidium-sodium compound is of only sparing solubility, and the cæsium-sodium salt is very insoluble. The thallium salt is not particularly soluble, and can easily be prepared in the pure state.

The ammonium-sodium, rubidium-sodium, and cæsium sodium salts have, as previously mentioned, been described in earlier papers, but some further methods of preparation, etc., are included here.

Ammonium Sodium Bismuthinitrite.

As previously prepared, this salt was obtained by dissolving solid bismuth nitrate in a cold, very concentrated solution of ammonium nitrate, and pouring the resulting liquid into a cold, nearly saturated solution of sodium nitrite. Analyses of the bright yellow powder obtained pointed to the formula $(NH_4)_2NaBi(NO_2)_6$. Subsequently, it has been prepared by adding a concentrated solution of ammonium nitrate to a concentrated solution of sodium nitrite containing bismuth. In order to prepare it in this manner, about 16 grams of the nitrite are dissolved in the least possible amount of water at the ordinary temperature, 5 c.c. of the bismuth nitrate solution are added, the mixture cooled with ice, and the compound precipitated by the addition of a previously-cooled solution of 4 grams of ammonium nitrate in about 5 c.c. of water. The yellow precipitate is collected after a few minutes, and dried as previously described. It is identical in appearance with the product obtained by the former method, and under the microscope appears homogeneous On analysis, however, the percentage of ammonium was found to be 6·04 and that of sodium 5·17. The ratio between these numbers is 1·17, and that between $3(NH_4)$ and 2Na is 1·176, pointing to the formula $9(NH_4),6Na,5Bi(NO_2)_6$ for the salt prepared in this way. This formula would require $NH_4=5{\cdot}97$ and $Na=5{\cdot}07$ per cent. (compare the case of the cæsium-sodium salt, given below). This and the succeeding salt can only be prepared from such concentrated solutions that it is very difficult to remove all mother liquor and ensure that a pure substance is being dealt with.

Potassium Sodium Bismuthinitrite.

This salt was at first thought to be incapable of existence, as on adding bismuth nitrate to a very concentrated solution of equal parts of the mixed nitrites of sodium and potassium, the substance deposited consisted of orange-yellow plates of potassium bismuthinitrite. It was found, however, that if a concentrated solution of potassium nitrite was gradually added to a concentrated solution of sodium nitrite containing bismuth, when a cetrain amount of the potassium salt had been added, bright yellow, octahedral crystals deposited, containing occasionally a few much larger, orange-coloured plates of potassium bismuthinitrite. These, if present, could be removed and a homogeneous product obtained.

To 20 grams of sodium nitrite are added 20 c.c. of water and 5 c.c. of the bismuth nitrate solution. The mixture is cooled to 0°, and any sodium nitrate that may deposit is filtered off. Into this liquid is poured a solution of 5 grams of potassium nitrite in about 5 c.c. of water, and the whole cooled to 0°. Should no precipitate form, a further small addition of potassium nitrite is made. After about half an hour the very finely-divided, yellow precipitate is collected, and as much as possible of the remaining mother liquor carefully removed by pressure on a porous plate.

The salt is a finely-divided powder, consisting of very small, bright yellow crystals, probably octahedral. The substance is unstable, and water at once hydrolyses it, although very small quantities of water produce a yellow solution.

On analysis the percentage of potassium found was 13·4, whilst the amount required by the formula $K_2NaBi(NO_2)_6$ is also 13·4. The percentage of NO_2 found was, however, much below the required quantity, being 43·6 as against 47·2. This may have been partly due to decomposition, but the formula $K_2NaBi(NO_2)_6$ can only be regarded, from these results, as probable, but not certain.

Rubidium Sodium Bismuthinitrite, $Rb_2NaBi(NO_2)_6$.

This salt has been previously described by one of the authors, and it is sufficient to mention here that it is best prepared as a bright yellow, crystalline precipitate by adding rubidium nitrate to a 15 per cent. solution of sodium nitrite containing bismuth. It is also formed in the reverse manner from rubidium nitrite by adding first bismuth nitrate, then sodium nitrite.

Caesium Sodium Bismuthinitrite.

The properties of this salt, and its use as a means of determining sodium gravimetrically, have been described by one of the present

authors in a former paper, and the salt is also referred to on p. 2112 of this paper. Like the ammonium–sodium compound, its composition appears to vary somewhat with the method of preparation. When prepared by adding a sodium salt to a solution of potassium nitrite containing bismuth and cæsium, the ratio between the cæsium and sodium in the salt was found to be 3Cs : 2Na, pointing to the formula $9CsNO_2,6NaNO_2,5Bi(NO_2)_3$, but a sample made in absence of potassium nitrite contained an amount of cæsium corresponding with the normal formula:

$$Cs_2NaBi(NO_2)_6.$$

Thallium Sodium Bismuthinitrite, $Tl_2NaBi(NO_2)_6,H_2O$.

To 25 c.c. of a 50 per cent. solution of sodium nitrite are added 5 c.c. of the bismuth nitrate solution, and then 1 or 2 grams of thallium nitrate or acetate in about 20 c.c. of water. The bright yellow crystals are collected after about an hour, and dried as previously described.

The salt forms fairly large, honey-yellow crystals, which are moderately stable on keeping, but are decomposed gradually when heated to 100°.

Found: Tl = 43·86; Na = 2·82; Bi = 22·36.

$Tl_2NaBi(NO_2)_6,H_2O$ requires Tl = 43·73; Na = 2·47; Bi = 22·30 per cent.

Another specimen, prepared in a very similar manner, did not contain any water, and was quite stable.

PART III.

Bismuthinitrites containing Nickel.

When nickel nitrate is added to solutions of the nitrites of sodium or of lithium containing bismuth, no precipitate is formed. On the addition of a salt of any of the metals of the X class a brownish-yellow or brownish-red precipitate of a mixed bismuthinitrite of the metal X and nickel is formed. These substances deposit slowly, and are micro-crystalline. They are produced with very small amounts of nickel. Owing to lack of time, these compounds were not fully investigated, but rather complex ratios were found on analysis between the metal X and nickel contained in them. Possibly this may be due to the substances consisting of mixtures of closely similar compounds containing a metal X and nickel in different ratios.

Ammonium Nickel Bismuthinitrite.

To 40 c.c. of a 50 per cent. solution of sodium nitrite are added 10 c.c. of the bismuth nitrate solution, and then to the mixture

cooled with ice a solution of 5 grams of ammonium nitrate and 2 grams of nickel nitrate in 20 c.c. of water. After a few minutes the reddish-yellow precipitate is collected and dried in the usual way.

The substance forms a yellowish-brown, micro-crystalline powder. It is very unstable, slowly evolving oxides of nitrogen, and water decomposes it immediately. It has not been possible to assign a definite formula to the substance, as the composition of different specimens varied considerably.

Found: $NH_4=6·05$, $6·45$; $Ni=4·16$, $3·59$; $Bi=32·9$; $NO_2=50·0$ per cent.

The substance also contained some water.

Potassium Nickel Bismuthinitrite.

To 40 c.c. of a 50 per cent. solution of potassium nitrite are added 5 c.c. of the bismuth nitrate solution, and then about a gram of nickel nitrate in 10 c.c. of water. Much of the precipitate deposits on the walls of the vessel. It is collected and dried in the usual manner.

This salt is a yellowish-brown, micro-crystalline powder, very similar to the nickel–ammonium salt, and, like it, very unstable.

As the salt decomposed gradually while being dried, giving off oxides of nitrogen, the value obtained for the (NO_2) is too low. The ratio between the bismuth and nickel in the salt is not affected by this decomposition. It was found to be 7·39, whereas the ratio 2Bi : Ni is 7·09.

Found: $Ni=4·25$; $Bi=31·4$; $NO_2=43·7$ per cent.

The compound approximates to the composition $K_4Ni,2Bi(NO_2)_6$, plus about 6 molecules of water.

Rubidium Nickel Bismuthinitrite.

This is prepared in a similar manner to the corresponding potassium compound, nickel nitrate, and then bismuth nitrate being added to a solution of rubidium nitrite.

It is a reddish-yellow powder consisting of minute crystals, which are less soluble and much more stable than the potassium salt. As this salt could be kept for some time, it was analysed fully, and the results are, no doubt, more correct than those obtained with the two previous salts which are difficult to analyse on account of their instability.

Found: $Rb=29·0$; $Ni=2·75$; $Bi=28·0$; $NO_2=37·14$; H_2O(by difference)$=3·11$.

The formula which corresponds most nearly with these numbers is $Rb_7Ni3\{Bi(NO_2)_6\},4H_2O$, for the ratio of Rb to Ni from the above numbers is 10·5, whilst the atomic ratio 7Rb : Ni is 10·2. This formula requires $Rb=27·4$; $Ni=2·69$; $Bi=28·6$; $NO_2=38·0$; $H_2O=3·30$ per cent.

The NO_2/Bi ratio is $37·14/28·0=1·326$, whilst the ratio $6NO_2/Bi=276/208=1·327$.

Caesium Nickel Bismuthinitrite.

This is prepared in the same manner as the rubidium salt (the nickel nitrate must be added before the bismuth nitrate, otherwise cæsium bismuthinitrite will precipitate), and resembles it closely in appearance and properties.

Found: $Cs=36·6$; $NO_2=32·6$.

These figures would indicate a formula similar to that of the rubidium-nickel salt, for the ratio of Cs to $NO_2=36·6/32·6=1·12$, whilst that of 7Cs to $18NO_2$, required by the formula

$$Cs_7Ni3\{Bi(NO_2)_6\},$$

is 1·12. The numbers agree most closely with the formula

$$Cs_7Ni3\{Bi(NO_2)_6\},6H_2O,$$

which would require $Cs=36·5$; $NO_2=32·5$ per cent.

Thallium Nickel Bismuthinitrite.

Fifteen grams of sodium nitrite are dissolved in about 60 c.c. of water, and 5 c.c. of the bismuth nitrate solution are added, as well as a few drops of acetic acid and 1 or 2 grams of nickel nitrate. A solution of 2 grams of thallium nitrate in about 40 c.c. of water is now added, when the substance is precipitated at once as a fine, red powder. This is collected after an hour or so, and dried as previously described.

The salt is a reddish-brown, crystalline powder, which is insoluble and decomposed slowly by water. It appears to be quite stable.

Found: $Tl=46·54$; $Ni=3·23$.

$Tl_4Ni,2Bi(NO_2)_6$ requires $Tl=44·28$; $Ni=3·13$ per cent.

Methods of Analysis.

In order to estimate the bismuth in these compounds the nitrite present was expelled by boiling with hydrochloric acid, the bismuth then precipitated with hydrogen sulphide, the sulphide dissolved in nitric acid, and the solution precipitated with ammonium carbonate, the precipitate being ignited and weighed as the trioxide.

Bismuth and silver were separated by precipitation of the silver with a slight excess of hydrochloric acid in the presence of much nitric acid.

Thallium and bismuth were separated by dissolving the salt in dilute hydrochloric or sulphuric acid, and then precipitating the bismuth as sulphide (the precipitate may contain a little thallium, which was separated by the method described by Crookes "Select Methods"). In the case of thallous silver bismuthinitrite, where the three metals are present together, the silver and bismuth were co-precipitated as sulphides from a solution in dilute sulphuric acid, and then separated by dissolving the sulphides in nitric acid (the nitric acid used in this case was more concentrated than that used for dissolution of bismuth sulphide alone, as the silver sulphide dissolved with difficulty) and precipitating the silver as chloride.

The thallium was determined generally by oxidation with decinormal permanganate, at a little below 100°, in the presence of hydrochloric acid, the thallium solution having been previously boiled with sulphurous acid to ensure the absence of thallic salts (Crookes, "Select Methods").

Thallium was also, in a few cases, determined as thallous iodide.

In the analysis of thallium nickel bismuthinitrite the salt was boiled with hydrochloric acid and much water to avoid precipitation of thallous chloride; the bismuth separated as sulphide, and the filtrate containing the nickel and thallium divided into two equal portions. To one of these was added some sulphurous acid, and the liquid boiled for some time. On titration with permanganate, 16·52 parts per cent. of thallium were found. The nickel and thallium in the other portion were separated by sodium carbonate, the thallium remaining in solution. After removal of the nickel this portion was treated exactly as the former one, and gave 16·55 per cent. of thallium. The nickel present, therefore, did not interfere with the estimation of the thallium with permanganate.

Nickel was estimated either as the dimethylglyoxime compound or as the monoxide after precipitation as peroxide. It was separated from the alkalis either by ammonium sulphide or dimethylglyoxime.

After the heavy metals had been removed by the methods indicated, cæsium, rubidium, and potassium were estimated as platinichlorides or as sulphates, lithium as sulphate, sodium as sulphate or as sodium cæsium bismuthinitrite. When two of the alkali metals were present at the same time, such as cæsium and lithium, the cæsium was estimated as platinichloride in one portion, and the cæsium and lithium together as sulphates in another portion, the lithium being then determined by difference.

The determination of ammonium in these compounds must be made very carefully, or the results will be too low, presumably owing to interaction between the NH_4 and NO_2 groups. A weighed quantity of the substance is dropped into *cold* fairly dilute sodium

hydroxide solution, and the ammonia then distilled off in a current of steam.

Nitrite was determined by oxidation with permanganate in the following manner: Distilled water acidified with sulphuric acid so as to contain about 1 per cent. of the acid was well boiled to expel air, and then cooled to 0°. A bottle holding about half a litre was nearly filled with the cooled acidified water, and enough permanganate added to give the liquid a just perceptible pink tint. About one and a-half times the required quantity of $N/10$-permanganate was now run into the bottle, and a weighed amount of the substance, not much greater than 0·1 gram, added in a small tube. The bottle was well shaken, and when all solid particles had disappeared, the excess of permanganate was estimated by means of a ferrous sulphate solution.

The determination has to be made with care, but gives very satisfactory results unless the compound also contains thallium, in which case, as has been previously mentioned in this paper (see p. 2127), the thallium is also partly oxidised.

The thanks of the authors are due to the Chemical Society for a grant from the Research Fund, which has defrayed the greater part of the cost of the above work, and to the managers of the Davy Faraday Research Laboratory for permission to conduct the work there.

THE DAVY-FARADAY RESEARCH LABORATORY,
ALBEMARLE ST., W.

CCXXV.—*The Nitrites of Thallium, Lithium, Caesium, and Rubidium.*

By WALTER CRAVEN BALL and HAROLD HELLING ABRAM.

THE nitrites of these metals appear to have been but incompletely examined, and as they were required in somewhat large quantities during an investigation on the bismuthinitrites, the authors thought that it would be of interest to record some points with regard to their preparation and properties.

Caesium Nitrite.

Cæsium nitrite has been prepared by G. S. Jamieson (*Amer. Chem. J.*, 1907, **38**, 616), and our preparations agreed in all

respects with his description, the salt being very soluble, hygroscopic, indistinctly crystalline, and possessing a faint yellow colour; in fact, resembling potassium nitrite very closely. Jamieson prepared the substance by the interaction of cæsium chloride and silver nitrite, and he mentions the difficulty of ensuring that this action shall be complete, unless the silver nitrite be wholly in solution. As silver nitrite is a sparingly soluble salt, a large volume of water is required, and the method is a tedious one. We discarded it in favour of the preparation from cæsium sulphate and barium nitrite, both of which are readily soluble salts. Barium nitrite can be bought in the pure state as the monohydrate $Ba(NO_2)_2,H_2O$, and solutions of this salt and of cæsium sulphate in equivalent proportions were heated and mixed, the barium sulphate removed by filtration, and the resulting solution of cæsium nitrite evaporated. This method is less costly and troublesome, and much more rapid, than that by way of silver nitrite.

Rubidium Nitrite.

This salt does not appear to have been previously described. It was obtained both from rubidium chloride and silver nitrite, and also by the interaction of the sulphate and barium nitrite, the latter method being, for the reasons given above, the better. The salt resembles the nitrites of cæsium and potassium very closely, forming an indistinctly crystalline mass of a pale yellow tint. It is deliquescent, and very soluble in water, as 50 grams of the salt dissolved readily in about 35 c.c. of water, forming a rather viscous solution. It is only sparingly soluble in hot absolute alcohol, and almost insoluble in acetone. The addition of absolute alcohol to a concentrated aqueous solution produces at first a separation of the mixture into two layers, the heavier one containing nearly all of the salt, just as in the case of potassium nitrite. On shaking this layer with more absolute alcohol, the solid separates.

Found: Rb = 65·2; NO_2 = 34·7.

$RbNO_2$ requires Rb = 65·0; NO_2 = 35·0 per cent.

The salt was dried at 170° before analysis as it retained a little water when dried at 100°.

Thallous Nitrite.

This substance does not appear to have been described before. We obtained it by dissolving thallium in a mixture of nitric and sulphuric acids, the sulphuric acid being present in only slight excess of the theoretical amount required to form thallous sulphate, and the nitric acid serving to dissolve the metal more rapidly.

The liquid was then evaporated, and the solid residue heated to expel the nitric acid. The product consisted chiefly of thallous sulphate, but contained also the thallic salt. It was necessary to reduce the whole to the thallous state; otherwise, on adding barium nitrite to produce thallous nitrite, the thallic salt present would oxidise some nitrite, and a mixture of thallous nitrite and nitrate result, which could not easily be separated into its constituents. The mixture of thallous and thallic sulphate was therefore boiled with excess of sulphurous acid, and the pure thallous sulphate crystallised out. This was recrystallised, dissolved in warm water, and treated with the requisite amount of barium nitrite. After removing the barium sulphate, the pale yellow filtrate was evaporated in a vacuum over sulphuric acid, or simply on the water-bath. Evaporation over sulphuric acid is the better plan, as the product forms more distinct crystals, and there is no chance of oxidation to nitrate, which possibly occurs to a slight extent when the solution is evaporated on the water-bath.

Thallous nitrite, $TlNO_2$, forms a soft, crystalline mass of a deep orange-red colour. When viewed under the microscope, the separate crystals are fairly large, but of indistinct shape, the edges generally seeming rounded; some of the crystals have the appearance of solidified drops. It melts very readily, without decomposition, to an orange-coloured liquid, and at a higher temperature evolves red fumes and leaves a pale yellow residue, probably chiefly thallous oxide, which dissolves partly in water to a strongly alkaline liquid. The salt is more soluble in water than the nitrate, for a solution was evaporated in a vacuum until it contained 27 grams per 100 c.c., and there was no sign of crystallisation. The strong aqueous solution is orange-yellow, but this colour rapidly disappears on dilution, and a dilute solution is almost colourless, the colour returning on concentration. It is insoluble in alcohol.

We did not attempt the preparation from thallous chloride and silver nitrite, as both these salts are only sparingly soluble.

The salt is anhydrous, as the following analyses show:

Found (mean of three analyses), $Tl=81{\cdot}6$.

$TlNO_2$ requires $Tl=81{\cdot}6$ per cent.

We were unable to discover a satisfactory method for the estimation of the nitrite radicle in the presence of thallium, and when the nitrite is estimated by permanganate at 0°, the thallium is also partly oxidised. The amount of oxygen taken up by the thallium is about two-thirds of that required for the oxidation to the thallic state when thallium alone is present, but rather more than this, about three-quarters, when the nitrite radicle is present also (this point is discussed further in the paper on "Bismuthi-

nitrites"). On the assumption that three-quarters of the theoretical amount of oxygen required for the complete oxidation of the thallium is taken up, then $TlNO_2$ would require 11·2 per cent. of its weight of oxygen for the complete oxidation of the NO_2 group plus the incomplete oxidation of the thallium. The amount found was 11·8 per cent. The formula $TlNO_2$ is therefore confirmed.

Lithium Nitrite.

This salt was stated by Lang to crystallise with half a molecule of water, and a formula representing this composition is given in the text-books. A short note by Rây (P., 1908, **24**, 75) states that it crystallises with one molecule of water. Our analyses confirm the formula $LiNO_2,H_2O$, and we have further examined this salt, and also anhydrous lithium nitrite. As in the case of the other nitrites described, it is more readily obtained from lithium sulphate and barium nitrite than from the chloride and silver nitrite, but we also prepared it by mixing equivalent amounts of lithium sulphate and potassium nitrite in very concentrated aqueous solution, evaporating considerably, removing by filtration the precipitate of potassium sulphate and lithium potassium sulphate, evaporating again until a dry residue was formed, and extracting this with absolute alcohol. Lithium nitrite is very soluble in absolute alcohol, whether present as $LiNO_2$ or as $LiNO_2,H_2O$, and as potassium nitrite is only very sparingly soluble in that solvent, the former salt is extracted in a nearly pure state. The alcoholic solution leaves, on evaporation, a white residue of small crystals, which, on the addition of a little water, changes to larger needle-shaped crystals of the monohydrate. When recrystallised once from absolute alcohol, the crystals contained only traces of potassium. The yield falls a good deal short of the theoretical, as part of the lithium is lost as potassium lithium sulphate, and, in consequence, some of the potassium nitrite is not acted on. Possibly sodium nitrite might be substituted for the potassium salt, but it would probably be more difficult to free the lithium nitrite from sodium nitrite than from potassium nitrite. Acetone might be used in place of alcohol in the above method of preparation, as it easily dissolves lithium nitrite.

The salt crystallises in flat, needle-shaped crystals, frequently 1 or 2 cm. in length. It appears to be white, having certainly less colour than the very feebly yellow-tinted sodium nitrite. It melts in its own water of crystallisation below 100°, and loses water slowly at this temperature. It is dehydrated more rapidly at 160°, losing also minute quantities of oxides of nitrogen, and leaving a residue, consisting almost entirely of the anhydrous salt, as a white

mass. It is very soluble in water, readily forming supersaturated solutions, from which crystals of $LiNO_2,H_2O$ deposit on adding a ready-formed crystal of the salt, or on cooling. A saturated solution must contain, at the ordinary temperature, about 90 grams of $LiNO_2,H_2O$ per 100 c.c., for a solution which contained 97 grams per 100 c.c. did not deposit any crystals on remaining for twenty-four hours at the ordinary temperature, but deposited approximately 6 grams per 100 c.c. after a small crystal of the salt had been added and the solution allowed to remain for some hours.

On adding a cobalt salt and a little acetic acid to a solution of lithium nitrite, a dark brown solution of lithium cobaltinitrite is formed, which, with cæsium, rubidium, potassium, and thallous salts, yields highly insoluble cobaltinitrites, just as does sodium cobaltinitrite.

The lithium nitrite used for analysis was prepared from the sulphate and barium nitrite. Before weighing, it was exposed in a desiccator over calcium chloride for about a month. Calcium chloride, therefore, does not dehydrate the salt:

0·1920 lost, on heating, 0·0493. $H_2O = 25·7$.

The dried residue, on ignition with sulphuric acid, gave 0·1471 Li_2SO_4. $Li = 9·7$.

0·0900 required 25·2 c.c. of $N/10$-potassium permanganate. $NO_2 = 64·4$.

$LiNO_2,H_2O$ requires $H_2O = 25·4$; $Li = 9·8$; $NO_2 = 64·9$ per cent.
$LiNO_2,\frac{1}{2}H_2O$ „ $H_2O = 14·6$; $Li = 11·2$; $NO_2 = 74·3$ „

The salt, dried over calcium chloride, is therefore the monohydrate.

It is interesting to note the great differences of colour between thallous nitrite and the other nitrites of the formula XNO_2; they all, with the possible exception of lithium nitrite, have a faint yellow tint, but thallium nitrite is deeply coloured. It appears to be the most deeply coloured of the simple nitrites of those metals which do not, as a rule, form coloured salts. Although silver, also a heavy metal, forms a nitrite of analogous composition, it is only feebly coloured. This deep colour of thallous nitrite might point to a difference from the other simple nitrites, and in this connexion one of the authors hopes to investigate the action of thallous nitrite on alkyl haloids.

Our thanks are due to the Chemical Society for a grant which defrayed part of the cost of this work, and to the Managers of the Davy-Faraday Research Laboratory, where it was carried out.

THE DAVY-FARADAY RESEARCH LABORATORY,
ALBEMARLE ST., W.

CCXXVI.—*The Catalytic Activity of Acids. Evaluation of the Activities of the Hydrogen Ion and the Undissociated Acid.*

By HARRY MEDFORTH DAWSON and FRANK POWIS.

THE view that the activity of acids in accelerating chemical change is due to the hydrogen ion rests to a large extent on the approximate proportionality between the relative catalysing powers and the corresponding values of the electrical conductivities of the acids. The velocity-coefficients used by Ostwald in making this comparison were those relating to the rate of inversion of sucrose or the rate of hydrolysis of esters.

At the time that this comparison was first instituted it was, however, recognised that the proportionality is by no means an exact one, and Ostwald supposed that the observed deviations were due to the interference of secondary factors of relatively small importance. Largely no doubt by reason of its simplicity, the theory that the catalytic activity of acids is essentially due to the hydrogen ion was accorded a most favourable reception, and for many years no serious attempt appears to have been made to challenge its validity. It is at any rate noteworthy that the efforts which were made to explain the anomalous variation of the activity of the mineral acids with concentration, and the influence of neutral salt on the activity of these acids, were not such as to bring into question the assumed relation between the velocity of the catalysed chemical change and the hydrogen-ion concentration of the catalysing acid.

In recent years the question of acid catalysis has entered into a new phase, and as a result of the accumulation of new observations and of increased accuracy in the measurement of reaction velocities, evidence has been obtained in support of the view that the catalysing power of an acid is not entirely due to the hydrogen ion, but that the undissociated acid also contributes to the observed effect.

Observations of Acree and Johnson (*Amer. Chem. J.*, 1907, **38**, [illegible]) on the rate of intramolecular transformation of acetylchloroaminobenzene led these authors to suggest that the catalysing acid is active in the non-ionised condition. The researches carried out by Goldschmidt on the velocity of esterification in alcoholic solution (compare *Zeitsch. physikal. Chem.*, 1910, **70**, 627; *Zeitsch. Elektrochem.*, 1911, **17**, 684; Goldschmidt and Thuesen, *Zeitsch. physikal. Chem.*, 1912, **81**, 30) have led to the expression of a similar opinion, and recent work on the rate of decomposition of methyl and ethyl diazoacetate in alcoholic solution (Bredig, Millar, and Braune,

Zeitsch. Elektrochem., 1912, **18**, 535; Snethlage, *ibid.*, p. 539, affords evidence which is distinctly favourable to the theory.

So far as aqueous solutions are concerned, the only two reactions which have been made use of in the investigation of the catalytic activity of acids and of the extent to which this varies with the acid concentration, with the temperature and pressure, and on the addition of the corresponding neutral salts, are the inversion of sucrose and the hydrolysis of esters. The latter reaction has been employed by Taylor (*Meddel. K. Vetensk. Nobelinstitut*, **2**, Nos. 34, 35, 37), whose observations relating to the influence of neutral salts and of varying concentration of the acid on the velocity of hydrolysis, are interpreted in terms of the theory that the catalytic effect is composite in character, being partly due to the hydrogen ion and partly to the undissociated acid.

If k_H denotes the catalytic activity of the hydrogen ion and k_M that of the undissociated acid, then from two experiments at different concentrations of the catalysing acid, or from two experiments with and without neutral salts in which the acid concentration is fixed, it is possible to evaluate k_H and k_M, provided that the degree of ionisation of the acid is known. The available data suffice to show that the ratio k_M/k_H varies very considerably from one acid to another, and that it decreases with the strength of the acid. In the case of the mineral acids, the ratio is greater than unity, and various observations seem to show that the activity of undissociated hydrogen chloride is about twice as great as that of the hydrogen ion. As yet, however, the accuracy attained in the evaluation of the ratio is very limited, and results obtained by different observers are not very consistent. The important question as to whether the ratio for a given acid is independent of the nature of the reaction which is catalytically accelerated has also not been answered in any satisfactory manner, although the data obtained by Taylor (*loc. cit.*) in experiments on the hydrolysis of different esters indicate that the ratio is independent of the nature of the ester.

The authors have now succeeded in obtaining experimental data which not only lend considerable support to the theory of the catalytic activity of the undissociated acid, but for the first time afford a means of determining with a fair degree of accuracy the catalysing powers of acids in the non-ionised condition.

The catalytically accelerated reaction made use of in these experiments was the isomeric transformation of acetone from the keto- to the enol-form, a reaction which takes place in aqueous solution with conveniently measurable velocity at 25°, and can be readily followed in the presence of iodine, which reacts very quickly with the enolic form (Dawson and Leslie, T., 1909, **95**, 1860). Under

vourable conditions the speed of this reaction is practically onstant, and in this respect the isomeric transformation of the etone possesses a distinct advantage over the two reactions (sugar version and ester hydrolysis) which have been mainly used in the xamination of the catalysing power of acids. This constancy in he rate of disappearance of the iodine is attained if the circumances are such that the concentration of the acetone is not appreciably altered during the progress of the reaction, and if the catalytic tivity of the hydriodic acid, which is formed as one of the final roducts of the reaction, is negligibly small in comparison with the tivity of the acid under investigation. In actual practice it is n easy matter to avoid the former source of disturbance, but the utocatalytic effect is more difficult to deal with when weak acids re under examination. In such cases the speed of the reaction creases continuously in consequence of the autocatalytic effect compare T., 1912, **101**, 1503), and it is necessary to eliminate this order to obtain the catalytic activity of the acid originally resent in the solution. The method finally adopted to attain this nd is very simple, and depends on the fact that the mean velocity f reaction during successive time intervals is a linear function f the mean concentration of the hydriodic acid which is liberated uring the progress of the reaction. All that is necessary, therefore, order to obtain the required initial velocity is to plot the served reaction-velocities for successive time intervals as ordinates gainst the corresponding mean concentrations of hydriodic acid s abscissæ and extrapolate to zero concentration of hydriodic acid. n example may be given to illustrate the influence of the autocatalytic effect, and also the method by which it has been eliminated. In this experiment the catalyst employed was 0·02 molar β-dibromopropionic acid, the concentration of the acetone 20 c.c. r litre (0·272 molar) and the original concentration of the iodine 0·394 mol. per litre. From time to time 25 c.c. of the reaction ixture were removed to a flask containing sodium acetate in cess of the quantity of acid used as catalyst, and titrated with shly standardised sodium thiosulphate solution of about 01 normality.

TABLE I.

No. of titration.	t (mins.).	Thiosulphate. c.c.	Iodine concentration (c). Mols. per litre.	Hydrogen iodide concentration. Mols. per litre.
1	0	21·40	0·003860	0·000080
2	100	18·74	0·003380	0·000560
3	270	14·02	0·002530	0·001410
4	430	9·29	0·001675	0·002265
5	530	6·22	0·001122	0·002818

By suitably combining these data, the following results are obtained for the connexion between the rate at which the iodine disappears and the mean concentration of the hydriodic acid.

From combination of	1 and 2.	1 and 3.	2 and 3.	2 and 4	3 and 4.	3 and 5.	4 and 5.
Mean HI concentration	0·00032	$0{\cdot}0^{3}75$	$0{\cdot}0^{3}98$	$0{\cdot}0^{2}141$	$0{\cdot}0^{2}184$	$0{\cdot}0^{2}211$	$0{\cdot}0^{2}2$[illegible]
$-\Delta c/\Delta t \times 10^{6}$ ...	4·80	4·93	5·00	5·17	5·34	5·42	5·52

From these numbers we obtain by extrapolation an initial velocity $= 4{\cdot}69 \times 10^{-6}$ mols. per litre per min., and this represents the rate of change due to the catalytic action of 0·02 molar αβ-dibromopropionic acid.

In general, the acceleration due to the hydriodic acid formed increases as the ionisation-coefficient of the catalysing acid diminishes, and in the case of a given acid it increases with increasing dilution. By reducing the concentration of the iodine and increasing the quantity of the solution removed for titration, it has been found possible to determine the activity of moderately weak acids in dilute solution without difficulty.

A point to which reference should be made is the fact that all the solutions contained a certain amount of potassium iodide, the iodine being added to the reaction-mixture in the form of an iodide solution, in which the molar ratio KI/I_2 was approximately equal to 2. That the presence of potassium iodide is without measurable influence on the initial velocity of the reaction is shown by a comparison of the results obtained in experiments with monochloroacetic acid in 0·05 molar solution, in which the concentration of the potassium iodide was varied considerably. The results in question are grouped in table II.

TABLE II.

Iodine concentration. Mols. per litre.	Potassium iodide concentration. Mols. per litre.	Initial velocity.
0·004	0·008	$4{\cdot}55 \times 10^{-6}$
0·004	0·08	$4{\cdot}65 \times 10^{-6}$
0·0125	0·025	$4{\cdot}60 \times 10^{-6}$

The divergence of the values from the mean is probably not greater than can be accounted for on the basis of experimental error.

The results communicated in this paper have reference to the five acids—hydrochloric, dichloroacetic, αβ-dibromopropionic, monochloroacetic, and acetic—which form a series of gradually decreasing strength. In the tables which follow, the concentration of the catalysing acid (c) is indicated in the first column, the degree of

ionisation (α) in the second, the hydrogen ion concentration ($C_{H^{\cdot}}$) in the third, the initial velocity (v) * of the isomeric change in the fourth, whilst the fifth gives the ratio of the reaction-velocity to the total acid concentration, and the sixth the ratio of the velocity to the hydrogen-ion concentration. In the case of hydrochloric acid, the degree of ionisation at concentrations between 0·01 and 0·2 mol. per litre has been taken from the table given by Bray and Hunt (*J. Amer. Chem. Soc.*, 1911, **33**, 781), and that for the two more concentrated solutions from Ostwald's data, which have been reduced to the scale of Bray and Hunt's figures by comparing the two ionisation-concentration curves. For the other acids, the degree of ionisation is that calculated from the mass law by means of the ionisation-coefficients recorded in Kohlrausch and Holborn's tables.

TABLE III.

Hydrochloric Acid.

c.	α.	$C_{H^{\cdot}}$.	v.	v/c.	$v/C_{H^{\cdot}}$.
0·01	0·971	0·00971	4·48	448	461
0·02	0·959	0·01918	9·10	455	474
0·05	0·940	0·0470	22·9	458	487
0·1	0·921	0·0921	46·5	465	505
0·2	0·897	0·1794	95·3	476	531
0·5	0·858	0·429	243·0	486	566
1·0	0·792	0·792	515·0	515	650

Dichloroacetic Acid.

c.	α.	$C_{H^{\cdot}}$.	v.	v/c.	$v/C_{H^{\cdot}}$.
0·01	0·856	0·00856	4·10	410	479
0·02	0·769	0·0154	7·95	398	516
0·05	0·621	0·0311	18·1	362	582
0·1	0·503	0·0503	32·7	327	650
0·2	0·393	0·0786	59·6	298	758

αβ-Dibromopropionic Acid.

c.	α.	$C_{H^{\cdot}}$.	v.	v/c.	$v/C_{H^{\cdot}}$.
0·01	0·549	0·00549	2·75	275	500
0·02	0·435	0·00870	4·69	234·5	539
0·05	0·305	0·01525	8·98	179·5	589
0·1	0·2275	0·02275	14·65	146·5	641
0·2	0·167	0·0334	27·05	135	810

Monochloroacetic Acid.

c.	α.	$C_{H^{\cdot}}$.	v.	v/c.	$v/C_{H^{\cdot}}$.
0·05	0·161	0·00805	4·6	92	571
0·1	0·117	0·0117	7·6	76	650
0·2	0·0842	0·0168	11·9	59·5	708
0·5	0·0542	0·0271	23·8	47·6	878
1·0	0·0386	0·0386	40·1	40·1	1039

Acetic Acid.

c.	α.	$C_{H^{\cdot}}$.	v.	v/c.	$v/C_{H^{\cdot}}$.
0·1	0·01332	0·00133	0·72	7·2	540
0·2	0·00945	0·00189	1·20	6·0	635
0·5	0·00598	0·00299	2·07	4·14	690
1·0	0·00423	0·00423	3·35	3·35	790

* v = velocity in mols. per litre per min. $\times 10^6$.

From the values of the ratio v/C_H in the last column of the tables it is evident that in no case is there an approximation to constancy, but that for all five acids the ratio increases as the concentration increases. The observed variation indicates very definitely that the catalysing power of an acid is very far from being determined solely by the hydrogen-ion concentration of its solutions, and that in this respect there is no difference between the behaviour of strong and weak acids. On inspection of the values of the ratio of the reaction-velocity to the total acid concentration (v/c) it will be noted that this also increases with increasing concentration of the acid in the case of hydrochloric, but that it decreases with increasing concentration for the four remaining acids which have been examined.

The existence of these relations suggested that the chemical change is catalysed, not only by the hydrogen ion, but also by the non-ionised acid, and that the observed effect is the sum of the two separate effects. If c is the concentration of the catalysing acid, a its degree of ionisation, k_H and k_M the activities of the ionised and non-ionised acid, and v_H and v_M the velocities due to these components respectively, then $v_H = k_H ac$ and $v_M = k_M(1-a)c$. If, further, v is the measured velocity of the reaction, then

$$v = v_H + v_M = k_H ac + k_M(1-a)c,$$

and if at a different concentration c', at which the ionisation amounts to a', the corresponding reaction-velocities are v', v'_H, and v'_M, then

$$v' = v'_H + v'_M = k_H a'c' + k_M(1-a')c'.$$

From such a pair of equations it is possible to determine k_H and k_M, and this has been done for each of the five acids.

Apart from the varying accuracy of the experimental determination of the reaction-velocity at the different concentrations, it is apparent, from a consideration of these equations, that the most favourable conditions for the evaluation of k_H and k_M are obtained by the combination of two experiments in which the ratio of the component reaction-velocities undergoes the largest possible variation. On this account the experiments made with the highest and lowest concentrations of the catalysing acid have been utilised for the calculation of k_H and k_M in each of the five series. The values thus obtained, which are placed at the head of each of the following series of data, have then been utilised in the calculation of the reaction-velocities at the intermediate concentrations, and these numbers are recorded in the fourth column, the corresponding observed values being given in the fifth. The second and third columns give numbers which represent the component velocities due to the hydrogen ion and the undissociated acid respectively.

TABLE IV.

Hydrochloric Acid.

$k_H = 437$. $k_M = 811$.

Concentration.	v_H.	v_M.	v.	v_{obs}.
0·02	8·38	0·66	9·04	9·10
0·05	20·54	2·43	23·0	22·9
0·1	40·25	6·40	46·65	46·5
0·2	78·4	16·7	95·1	95·3
0·5	187·5	57·6	245	243

Dichloroacetic Acid.

$k_H = 445$. $k_M = 203$.

0·02	6·85	0·94	7·79	7·95
0·05	13·84	3·85	17·7	18·1
0·1	22·38	10·09	32·5	32·7

αβ-Dibromopropionic Acid.

$k_H = 449$. $k_M = 74$.

0·02	3·83	0·84	4·67	4·69
0·05	6·71	2·57	9·3	9·0
0·1	10·01	5·72	15·7	14·65

Monochloroacetic Acid.

$k_H = 448$. $k_M = 23·7$.

0·1	5·24	2·09	7·33	7·60
0·2	7·54	4·34	11·9	11·9
0·5	12·14	11·21	23·35	23·8

Acetic Acid.

$k_H = 425$. $k_M = 1·55$.

0·2	0·803	0·307	1·11	1·20
0·5	1·27	0·77	2·04	2·07

In a second series of experiments with monochloroacetic acid, the concentration of the acetone was 50 c.c. per litre. If the constants obtained ($k_H = 1055$ and $k_M = 59·6$) are reduced to a concentration of 20 c.c. per litre, the values obtained are $k_H = 422$ and $k_M = 23·8$. The latter is identical with the k_M value in the tabulated series of experiments, and the k_H values are not very different. A comparison of the observed and calculated values of the reaction-velocity in the previous table shows that the two series of numbers are, on the whole, in good agreement, and it cannot be denied that substantial evidence is thereby obtained in support of the view that the catalytic activity is due to the composite influence of the ionised and non-ionised acid.

The data for the five acids afford five independent values for the activity of the hydrogen ion, which are brought together in the following table.

TABLE V.

Nature of catalysing acid.	k_H.
Hydrochloric	437
Dichloroacetic	445
$\alpha\beta$-Dibromopropionic	440
Monochloroacetic	448
Acetic	425
Mean......	439, say 440

When the magnitude of the possible experimental error which is associated with the determination of the reaction velocities is taken into consideration, it must be admitted that the agreement between the individual values is remarkably good. If the mean value $k_H = 440$ is taken as representing the true activity of the hydrogen ion, it is possible to utilise all the available experimental data for the evaluation of the activities of the various acids in the non-ionised form. From each measurement of the reaction-velocity v, k_M will be obtained by means of the equation:

$$v = 440c\alpha + k_M c(1-\alpha).$$

The values thus deduced are collected in the following table, the particular experiment from which each number is obtained being indicated by reference to the concentration of the acid solution.

TABLE VI.

Nature of catalysing acid.	Calculated values of k_M. Mols. acid per litre. 0·01	0·02	0·05	0·1	0·2	0·5	1·0
Hydrochloric	725	805	740	755	795	765	800
Dichloroacetic	230	255	233	212	206	—	—
$\alpha\beta$-Dibromopropionic	74	76	65	60	74	—	—
Monochloroacetic	—	—	25·2	27·7	24·6	25·1	24·1
Acetic	—	—	—	1·36	1·87	1·50	1·49

The agreement between the k_M values obtained from the experiments at different acid concentrations is as good as that which could reasonably be anticipated when the nature of the experimental data and the probable error attaching to the reaction-velocity values is taken into account.

In consequence of the greater influence of the autocatalytic effect at the higher dilutions, it is probable that the degree of trustworthiness attaching to the several k_M values increases to some extent as the concentration increases. In deducing those values which have been adopted as the most probable values of

k_M, this circumstance has been taken into account as far as possible. The values referred to are recorded in the second column of the following table; in the third column is given the value k_M/k_H or the activity of undissociated acid in terms of that of the hydrogen ion.

TABLE VII.

Acid.	k_M.	k_M/k_H.	K.
Hydrochloric	780	1·77	—
Dichloroacetic	220	0·50	$5·1 \times 10^{-2}$
αβ-Dibromopropionic	67	0·152	$0·67 \times 10^{-2}$
Monochloroacetic	24·5	0·055	$0·155 \times 10^{-2}$
Acetic	1·50	0·0034	$0·0018 \times 10^{-2}$

It will be seen from the above table that the catalysing power of the undissociated acid diminishes rapidly as the ionisation tendency decreases, a relation which has already been pointed out by Snethlage (*loc. cit.*). As yet, however, it has not been possible to find any quantitative relationship between the activity of the undissociated acid and the specific affinity-coefficient, the values of which are recorded in the fourth column of the table.

It is of some interest to compare the values of k_M/k_H in the above table with those which have been calculated from observations on other catalysed reactions in aqueous solution. From Palmaer's data (*Zeitsch. physikal. Chem.*, 1897, **22**, 492) for the velocity of inversion of sucrose by hydrochloric acid at different concentrations, Snethlage has obtained $k_M/k_H = 2$. According to Taylor's observations on ester hydrolysis under the influence of hydrochloric acid (*loc. cit.*), the value of k_M/k_H is of the order of 3. Although these numbers can only be regarded as approximate, the order of magnitude of the activity ratio is in accord with the result obtained in our experiments.

From his experiments on the rate of hydrolysis of ethyl acetate with dichloroacetic acid as catalyst, Taylor has obtained $k_M/k_H =$ 0·16, 0·07, and 0·02 from three pairs of velocity measurements. In view of the wide divergence between the three values it might be argued that the experimental results in question are opposed to the existence of a velocity-coefficient characteristic of the undissociated acid. It is, however, much more probable that the divergence is due to experimental errors on the one hand and the unsuitability of the experiments as a combination on the other. If the arithmetic mean $k_M/k_H = 0·08$ is taken as an approximate measure of the relative activity of the undissociated acid, it is seen that this value is very much smaller than that obtained by us, for according to the previous table, the activity of the undissociated dichloroacetic acid is exactly one-half that of the hydrogen ion.

A third comparison which may be made has reference to acetic

acid, for which, according to Snethlage's calculation from Arrhenius' experiments on the inversion of sucrose, $k_M/k_H = 0{\cdot}006$. This is larger, but of the same order as the value obtained by us, $k_M/k_H = 0{\cdot}0034$.

The question as to whether the ratio k_M/k_H is independent of the nature of the catalysed reaction has already been discussed by Snethlage and by Taylor (*loc. cit.*). According to Snethlage, the ratio is practically independent of the nature of the solvent as well as of the catalysed reaction, and is mainly determined by the magnitude of the ionisation-coefficient of the acid.* In our opinion the available experimental material is not nearly sufficient to permit of the expression of any definite opinion with regard to the connexion between k_M/k_H and the nature of the catalysed reaction. On the one hand, the values of k_M/k_H for hydrochloric and acetic acid are approximately the same, whether these are deduced from experiments on the rate of isomeric change of acetone or the velocity of sucrose hydrolysis. On the other hand, the values of k_M/k_H for dichloroacetic acid appear to differ widely according to whether the rate of isomeric change of acetone or the rate of hydrolysis of ethyl acetate is the catalysed reaction. The evidence in respect of these three reactions is therefore quite inconclusive, and for the present we are scarcely justified in assuming that the activity ratios recorded in the previous table are independent of the nature of the change which has been made use of in these experiments.

In conclusion a comparison may be made between the observed reaction velocities and those calculated from the constants in the previous table (VII). The arrangement of the table is similar to that in table IV, except that a column is added giving the ratio of the velocity due to the non-ionised acid to that due to the hydrogen ions, that is, v_M/v_H, at each concentration.

TABLE VIII.

Hydrochloric Acid.

$k_H = 410$. $k_M = 780$.

Concentration. Mols./litre.	v_H.	v_M.	v_M/v_H.	v.	v_{obs}.
0·01	4·27	0·23	0·054	4·50	4·48
0·02	8·44	0·64	0·076	9·08	9·10
0·05	20·68	2·34	0·113	23·0	22·9
0·1	40·52	6·16	0·152	46·7	46·5
0·2	78·93	16·07	0·205	95·0	95·3
0·5	188·8	55·4	0·295	244	243
1·0	348·5	162·2	0·465	511	515

* We would point out that the ratio k_M/k_H for a given acid cannot be independent of the solvent if it is determined by the ionisation-coefficient, for the ionisation coefficient of an acid varies with the solvent.

Dichloroacetic Acid.

$k_H = 440.\quad k_M = 220.$

0·01	3·77	0·32	0·085	4·09	4·10
0·02	6·77	1·02	0·151	7·79	7·95
0·05	13·68	4·17	0·305	17·85	18·1
0·1	22·13	10·93	0·495	33·1	32·7
0·2	34·58	26·70	0·775	61·3	59·6

αβ-Dibromopropionic Acid.

$k_H = 440.\quad k_M = 67.$

0·01	2·42	0·30	0·125	2·72	2·75
0·02	3·83	0·76	0·20	4·59	4·69
0·05	6·71	2·33	0·345	9·04	8·98
0·1	10·01	5·17	0·515	15·2	14·65
0·2	14·70	11·16	0·76	25·85	27·05

Monochloroacetic Acid.

$k_H = 440.\quad k_M = 24·5.$

0·05	3·54	1·03	0·29	4·55	4·6
0·1	5·15	2·16	0·42	7·3	7·6
0·2	7·39	4·49	0·61	11·9	11·9
0·5	11·88	11·59	0·975	23·5	23·8
1·0	16·98	23·54	1·39	40·5	40·1

Acetic Acid.

$k_H = 440.\quad k_M = 1·50.$

0·1	0·585	0·15	0·255	0·73	0·72
0·2	0·83	0·30	0·36	1·13	1·20
0·5	1·32	0·75	0·57	2·07	2·07
1·0	1·86	1·49	0·80	3·35	3·35

The degree of concordance between the calculated and observed velocities of reaction recorded in the fifth and sixth columns is convincingly in favour of the view that the catalytic action of an acid is of composite character, and that it is additively determined by the activities of the ionised and non-ionised acid.

It is of interest to compare the magnitude of the effects due to the hydrogen ion and the undissociated acid as measured by v_H and v_M. As was to be expected, the relative importance of the undissociated acid increases with increasing concentration, and one instance is afforded by the experiments in which the catalytic effect of the undissociated acid is appreciably greater than that of the hydrogen ion. This relationship is found in the case of monochloroacetic acid in N-solution, where $v_M/v_H = 1·39$. Assuming that the mass law is applicable to the ionisation of weak acids in more concentrated solutions, it is possible to calculate the concentration at

which the observed catalytic effect is equally shared between the hydrogen ion and the non-ionised acid. This is the case when

$$k_M c(1-a) = k_H ca$$

that is,

$$k_M/k_H = a/(1-a).$$

The acid concentration at which the ratio $a/(1-a)$ is equal to k_M/k_H may be deduced from the ionisation-coefficient of the acid, and in this way the following values are obtained:

TABLE IX.

Dichloroacetic acid	0·31 mol. per litre.
$\alpha\beta$-Dibromopropionic acid	0·34 ,,
Monochloroacetic acid..................	0·52 ,,
Acetic acid	1·56 ,,

It is rather surprising to find that the concentrations for which the catalytic effects of the ionised and non-ionised acids are equal should be so close together, but this becomes intelligible if the rapid fall in the activity of the non-ionised acid with its tendency to ionise is taken into consideration.

Summary.

The catalytic activity of a series of acids has been investigated by experiments on the velocity of the keto-enol transformation of acetone. The variation of the catalysing power of the several acids with concentration can be very satisfactorily interpreted on the supposition that the observed effect is due to the sum of the catalytic activities of the ionised and non-ionised acids. The activity of the non-ionised acid has been determined in terms of that of the hydrogen ion, and it is found that this diminishes rapidly as the ionising tendency of the acid decreases.

The activity ratio k_M/k_H for hydrochloric and acetic acids has approximately the same value as the ratio obtained for these acids from observations on the hydrolysis of sucrose. It cannot yet be said, however, that this ratio is independent of the nature of the catalysed reaction.

The experiments afford instances of catalysis in which the effect of the undissociated acid is equal to, and even considerably greater than, that due to the hydrogen ion.

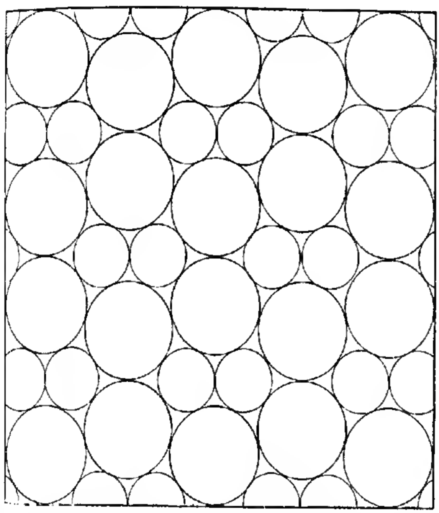
PHYSICAL CHEMISTRY LABORATORY,
THE UNIVERSITY, LEEDS.

CCXXVII.—*Contributions to the Theory of Solutions. The Intermiscibility of Liquids.*

By JOHN HOLMES.

It has often been pointed out that current theories afford little, if any, explanation of what may be called the simpler facts associated with solution, such as relative solubility, volume changes, heat production, etc. Previous investigations in this connexion have supported the view that physical forces alone are operative in

FIG. 1.



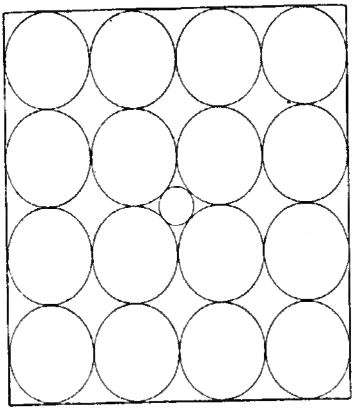
solution, and that the magnitude and extent of the accompanying phenomena are conditioned by the relative complexities of the molecules in the liquid state (T., 1906, **89**, 1781; 1907, **91**, 1608; 1909, **95**, 1919).

The liquid molecule is assumed to consist of a nucleus of great density representing the area of activity of its constituent atoms, and an outer envelope or sphere of influence, the extent of which depends on the magnitude of the resultant of electrical forces inherent in each atomic arrangement, and the consequent repulsive force between the envelopes of similar molecules.

From a purely mechanical point of view, and always assuming

absence of chemical change, any two liquids the molecular spheres of which have equal radii, should be miscible in all proportions. If, however, we have a binary mixture in which the spheres are of different sizes, then as the ratio of the radius of the larger to that of the smaller sphere increases, the dimensions of the interspaces also necessarily change, and a point is reached when the close packing of spheres is a maximum. In an equimolecular mixture this occurs when the radii are as 1·618 to 1 (Fig. 1). It is suggested that when these conditions are fulfilled the liquids are on the border line between complete as compared with partial miscibility, and that, so long as this or a smaller ratio exists, the

FIG. 2.



liquids will be mutually miscible. When, however, the ratio becomes greater than this value, a complex is formed which will not allow of the same close-packing, but results in the formation of two layers of liquid, in each of which the distribution of molecules depends on the further change in this ratio until it reaches 2·414, when, the smaller spheres being able to pass completely through the interspaces between the larger spheres (Fig. 2), the liquids should be now wholly immiscible.

The present investigation was undertaken to ascertain how closely these theoretical speculations agree with known facts.

From the curves of volume change calculated from the densities of aqueous mixtures of the lower primary alcohols it was deduced that the molecular complexity of water was the same as that of each of the alcohols (*loc. cit.*). In these circumstances the radii of the molecular spheres of methyl alcohol, ethyl alcohol, and *n*-propyl

ohol at 15° (represented by the cube roots of the quotients of lecular weight by density) are 1·31, 1·48, and 1·60 respectively, en compared with that of water as unity. These values are well thin the requirements of the above hypothesis in respect of scibility *inter se* and with water.

The butyl alcohols, however, are only partly miscible with water, d should have molecular radii proportionately greater than those the lower homologues, and greater also than that required theoically for partial miscibility, namely, 1·618. Assuming similar plexity, and taking the density at 20°/4° of *iso*butyl alcohol 0·8029 (Traube) and that of *n*-butyl alcohol as 0·8099 (Brühl), radii of the molecular spheres compared with that of water as ity (referred to the gaseous state) are 1·723 and 1·718 respecely. Since the coefficients of expansion of liquids differ invariy, the influence of change of temperature on a binary mixture st result in corresponding differences in the dimensions of the lecular spheres, and when the ratio of the respective radii proximates to 1·62 the same initial mixture would be expected be wholly or partly miscible according to the temperature. The ubility of water in *iso*butyl alcohol increases with rise of temrature, and an aqueous mixture containing 67·2 per cent. by ight of alcohol, corresponding with that required by the formula $H_{10}O,2H_2O$, is miscible at 113°, although at lower temperatures aration into layers occurs (Alexéev, *Ann. Phys. Chem.*, 1886, . 28, 305). These facts serve, therefore, to fix the complexities *iso*butyl alcohol as similar to those of water and the lower ohols.

Very similar results are given by the fatty acids which from ume change considerations are also found to have a similar plexity. Compared with water, the radii of formic acid, acetic id, propionic acid, and *n*-butyric acid are 1·28, 1·47, 1·60, and 2 respectively. Although *n*-butyric acid is miscible with water all proportions at the ordinary temperature, *iso*butyric acid has ly a limited miscibility. Since no data were available in respect

	(i).	(ii).	(iii).	(iv).	(v).
ight of *iso*butyric acid ...	26·7315	18·6841	25·2368	24·6530	24·0162
ight of water	3·9007	4·0278	5·7076	7·6157	9·3764
nsity of mixture at 15°/4°	0·97303	0·97806	0·97869	0·98292	0·98607
lume of *iso*butyric acid at 15°	28·043	19·601	26·475	25·863	25·194
lume of water at 15°	3·904	4·031	5·713	7·622	9·384
uivalent volume of water mixed with 100 volumes of acid at 15°	13·922	20·567	21·577	29·472	37·249
ntraction in volume when the volume of acid is constant at 100 volumes	1·662	2·095	2·155	2·535	2·837

of aqueous mixtures of the latter acid, the following mixtures were made and their relative densities determined at 15° in a pyknometer of about 25 c.c. capacity. The sample of *iso*butyric acid (Kahlbaum's) had a density 0·95323 at 15°/4° and boiling point 155·3°. Weights are reduced to vacuum.

These volume changes were plotted, and the following values obtained by interpolation:

Equimolecular Volumes at 15° (*gaseous*). $100C_4H_8O_2 : 19{\cdot}52H_2O$

(i). Molecular mixture. $C_4H_8O_2$.	H_2O.	(ii). Contraction in volume when the volume of acid is constant at 100 volumes.	(iii). Difference between the proportions by volume of acid in the initial and final volumes.
1	0·67	1·59	1·262
1	1·00	2·04	1·453
1	1·50	2·53	1·544
1	1·75	2·74	1·554
1	1·91	2·84	1·538

At lower concentrations these liquids are only partly miscible, but as seen from column iii, the difference between the proportions of *iso*butyric acid in the initial and final volumes reaches a maximum at a mixture approximating to that required by the formula $4C_4H_8O_2,7H_2O$. According to the method adopted in previous communications for determining relative complexities, this indicates that *iso*butyric acid and water are similarly complexed. The displacement of this point from equimolecular proportions is consequent on the above theory of spheres, for in a binary mixture the point of maximum difference in volume of the constituent possessing the greater molecular volume departs more and more from an equimolecular mixture as the ratio of the radii increases from unity to 1·618 when close-packing is a maximum, and beyond which the liquids cease to be miscible—assuming that no change in radii occurs on mixing.

As in the analogous case of aqueous *iso*butyl alcohol, the solubility of water in *iso*butyric acid increases with rise of temperature, and at 7·5° there is present 71 per cent. of acid, a quantity corresponding with that required by the formula $C_4H_8O_2,2H_2O$ (Rothmund, *Zeitsch. physikal. Chem.*, 1898, **26**, 475). Taking the density at 20°/4° of *iso*butyric acid as 0·9515, and that of *n*-butyric acid as 0·9587 (Brühl), the radii of the molecular spheres of these acids compared with that of water are 1·725 and 1·720 respectively. These values are very simliar to those given above for the butyl alcohols, and the relatively greater solubility factors of the acids in water are due probably to greater contraction in volume on admixture and consequent change in radii.

These results render it probable that our hypothetical assump-

tions approximate to a true representation of the facts, and that a knowledge of density and relative solubility may suffice for ascertaining molecular complexity in the liquid state. By taking as basis the similar complexity of the homologous series of primary alcohols, fatty acids, and water, together with the fact that diminishing solubility is indicative of greater molecular volume, the determination of the complexities of other liquids would appear to present little difficulty.

Acetone.—Acetone is miscible with water in all proportions and also with the less soluble higher alcohols. According to the above theory, its molecular volume should be greater than that of water, but less than that of the butyl alcohols. The following values are calculated from McElroy's data for densities of aqueous acetone mixtures at 20° (*Amer. Chem. J.*, 1894, **16**, 618).

Equimolecular Volumes (gaseous). $100C_3H_6O : 24{\cdot}6H_2O$.

(i).	(ii).	(iii) (ΔC_3H_6O).
$2C_3H_6O,H_2O$	$-2{\cdot}28$	1·84
$1\frac{1}{2}C_3H_6O,H_2O$	$-2{\cdot}80$	2·12
C_3H_6O,H_2O	$-3{\cdot}70$	2·48
$C_3H_6O,1\frac{1}{2}H_2O$	$-4{\cdot}96$	2·74
$C_3H_6O,2H_2O$	$-5{\cdot}88$	2·71
$C_3H_6O,3H_2O$	$-7{\cdot}03$	2·42

In these and following mixtures the molecular mixture is given in column i; column ii gives the change in volume when the volume of the particular liquid in question (in this case acetone) is constant at 100 volumes, the signs + and − referring to expansion and contraction respectively; column iii refers to differences (Δ) between the proportion by volume of this liquid in the initial and final volumes.

The greatest difference between the proportion by volume of acetone before and after mixing occurs at the molecular mixture $C_3H_6O,1\frac{1}{2}H_2O$. This result is similar to those obtained in aqueous *n*-propyl alcohol and propionic acid mixtures, and indicates that the acetone molecule is similarly complexed to that of water. The ratio of the radii of the respective molecules at 20° is therefore as 1·59 to 1.

Pyridine.—The following values are calculated from densities of aqueous mixtures of pyridine at 15·5° (Holmes, T., 1906, **89**, 1784).

Equimolecular Volumes (gaseous). $100C_5H_5N : 22{\cdot}5H_2O$.

(i).	(ii).	(iii) (ΔC_5H_5N).
$2C_5H_5N,H_2O$	$-1{\cdot}12$	0·91
$1\frac{1}{2}C_5H_5N,H_2O$	$-1{\cdot}43$	1·09
C_5H_5N,H_2O	$-1{\cdot}95$	1·32
$C_5H_5N,1\frac{1}{2}H_2O$	$-2{\cdot}47$	1·41
$C_5H_5N,2H_2O$	$-2{\cdot}80$	1·35
$C_5H_5N,3H_2O$	$-3{\cdot}17$	1·15

Here, again, ΔC_5H_5N is a maximum for the mixture $C_5H_5N,1\frac{1}{2}H_2O$. Pyridine is miscible with water in all proportions and with most other liquids; like acetone, its molecular volume should lie between those of water and the butyl alcohols. Assuming similar complexity as indicated by the above volume-changes, the ratio of the radius of the pyridine molecule to that of water is 1·64, a value supported by the displacement of the point of greatest difference (Δ).

Nicotine.—Nicotine also is miscible with most liquids at the ordinary temperature, and the radius of its molecular sphere should approximate to that of pyridine. The following values are calculated from Pribram's data for aqueous nicotine mixtures at 20° (*Sitzungsber. K. Akad. Wiss. Wien*, 1897, ii*b*, 106).

Equimolecular Volumes (gaseous). $100C_{10}H_{14}N_2 : 11{\cdot}24H_2O$

(i).	(ii).	(iii) ($\Delta C_{10}H_{14}N_2$).
$C_{10}H_{14}N_2,H_2O$	−1·88	1·545
$C_{10}H_{14}N_2,1\frac{1}{2}H_2O$	−2·62	1·963
$C_{10}H_{14}N_2,2H_2O$	−3·20	2·190
$C_{10}H_{14}N_2,2\frac{1}{2}H_2O$	−3·70	2·322
$C_{10}H_{14}N_2,3H_2O$	−4·17	2·407
$C_{10}H_{14}N_2,3\frac{1}{2}H_2O$	−4·45	2·368
$C_{10}H_{14}N_2,4H_2O$	−4·75	2·338

It is evident that these results differ materially from any obtained hitherto, inasmuch as the greatest difference between the percentage of nicotine in the initial and final volumes occurs at a mixture well removed from equimolecular proportions referred to the gaseous state. From the above figures the complexity of nicotine would appear to be one-half of that of water, and the equimolecular *liquid* mixture $C_{10}H_{14}N_2,2H_2O$. As in the case of pyridine and water, the maximum difference is removed to the mixture $C_{10}H_{14}N_2,1\frac{1}{2}(H_2O)_2$, indicating proximity to the series of liquids only partly miscible with water.

A similar complexity for nicotine is deducible from its mixtures with methyl alcohol at 20° (Winther, *Zeitsch. physikal. Chem.*, 1907, **60**, 563).

Equimolecular Volumes (gaseous). $100C_{10}H_{14}N_2 : 25{\cdot}14CH_4O$.

(i).	(ii).	(iii) ($\Delta C_{10}H_{14}N_2$).
$C_{10}H_{14}N_2,CH_4O$	1·15	0·712
$C_{10}H_{14}N_2,1\frac{1}{2}CH_4O$	−1·58	0·843
$C_{10}H_{14}N_2,2CH_4O$	−1·93	0·866
$C_{10}H_{14}N_2,2\frac{1}{2}CH_4O$	−2·20	0·841
$C_{10}H_{14}N_2,3CH_4O$	2·45	0·808

Assuming similar complexity, the ratio of the radius of the nicotine molecule to that of water as unity at 20° would be

$$\sqrt[3]{\frac{162{\cdot}132}{1{\cdot}00995}} \div \sqrt[3]{\frac{18{\cdot}016}{0{\cdot}99823}} \text{ or } 2{\cdot}07.$$

If our hypothesis is correct, this value is impossible for a liquid

hich is miscible with water in all proportions. By taking, however, the complexity of nicotine as one-half of that of water, the tio of radii becomes 1·64, a value which is consistent with its lative solubility.

Below 60°, nicotine and water are miscible in all proportions, but t higher temperatures two layers separate (Hudson, *Zeitsch. hysikal. Chem.*, 1904, **47**, 114). A sample of nicotine was purified nd fractionated under diminished pressure, and its density deter-ined at different temperatures in Sprengel pyknometers of 20 c.c. apacity. An aqueous mixture was prepared containing 69·23 per ent. of nicotine as required by the formula $C_{10}H_{14}N_2,2(H_2O)_2$, or ne molecule of nicotine with two molecules of water in the liquid tate, and the temperature determined at which partial miscibility ommenced. The mixture contained 20·4844 grams of nicotine and ·1038 grams of water. When heated in a sealed tube it remained omogeneous until a temperature of 75·8° was reached, when a loudiness appeared at the surface; at 76·0° this had spread hrough the mass of liquid, and two layers separated. Compared ith water at 4°, the densities of nicotine at 26·1°, 73·3°, 74°, and 9·4° were found to be 1·0064, 0·9685, 0·96797, and 0·9552 respec-ively, and that of the aqueous mixture at 74° was 0·98965.

The initial volumes of nicotine and water in the mixture at 74° re 21·162 c.c. and 9·333 c.c., and the final volume 29·898 c.c., or 0 volumes of nicotine when mixed with 44·10 volumes of water ontract to the extent of 2·82 volumes, so that at this temperature he volume change is still considerable (compare p. 2152).

The ratios of the radii of the nicotine and water spheres increase ith rise of temperature, and at 26·1°, 73·3°, and 89·8° are 1·64, 65, and 1·66 respectively. These values are so close to that equired theoretically for partial miscibility that they may be emed sufficient confirmation of the complexity found above for icotine, namely, one-half of that of water.

Ethyl Ether.—Ethyl ether is only partly miscible with water, ut miscible in all proportions with the lower primary alcohols. he radius of its molecular sphere compared with that of water hould lie between 1·62 and 2·41. The following values are calcu-ated from Baker's recent data for densities of mixtures of ethyl ther with methyl alcohol at 25° (T., 1912, **101**, 411).

Equimolecular Volumes (gaseous). $100C_4H_{10}O : 38{\cdot}82CH_4O$.

(i).	(ii).	(iii) ($\Delta C_4H_{10}O$).
$3C_4H_{10}O,CH_4O$	−0·74	0·58
$2C_4H_{10}O,CH_4O$	−0·99	0·70
$C_4H_{10}O,CH_4O$	−1·45	0·76
$C_4H_{10}O,1\frac{1}{2}CH_4O$	−1·76	0·71
$C_4H_{10}O,2CH_4O$	−1·98	0·63
$C_4H_{10}O,3CH_4O$	−2·27	0·49

These figures indicate that ethyl ether is similarly complexed to water. The molecular volumes of these liquids at 25° are therefore as 5·80 to 1, with a corresponding ratio of radii 1·80.

Aniline.—According to Alexéev (*loc. cit.*), aniline and water are miscible in all proportions above 167°. Below this temperature they are only partly miscible, the aniline layer containing more aniline as the temperature falls. The complexity of aniline is readily determined from the curves of volume-change calculated from the densities of its mixtures with the lower alcohols.

Aniline-Ethyl Alcohol Mixtures at 16·3° (Jöhst, *Ann. Phys. Chem.*, 1883, [iii], **20**, 56).

Equimolecular Volumes (gaseous). $100C_6H_7N : 62{\cdot}72C_2H_6O$

(i).	(ii).	(iii) (ΔC_6H_7N).
$4C_6H_7N,C_2H_6O$	−0·37	0·28
$2C_6H_7N,C_2H_6O$	−0·71	0·41
C_6H_7N,C_2H_6O	−1·13	0·43
$C_6H_7N,2C_2H_6O$	−1·48	0·29
$C_6H_7N,4C_2H_6O$	−1·62	0·13

Aniline–Methyl Alcohol Mixtures at 25° (Holmes and Sageman, T., 1909, **95**, 1933).

Equimolecular Volumes (gaseous). $100C_6H_7N : 44{\cdot}42CH_4O$.

(i).	(ii).	(iii) (ΔC_6H_7N).
$2C_6H_7N,CH_4O$	−1·15	0·78
$2C_6H_7N,1\frac{1}{2}CH_4O$	−1·57	0·89
C_6H_7N,CH_4O	−1·93	0·94
$C_6H_7N,1\frac{1}{4}CH_4O$	−2·25	0·94
$C_6H_7N,1\frac{1}{2}CH_4O$	−2·53	0·92
$C_6H_7N,1\frac{3}{4}CH_4O$	−2·77	0·89
$C_6H_7N,2CH_4O$	−2·99	0·85

These results indicate that aniline has a complexity similar to that of the primary alcohols.

Interpolating from Alexéev's curve of saturation, the critical temperature of solution for the molecular mixture $C_6H_7N,2H_2O$ requiring 72·1 per cent. of aniline, is 158°. The density of aniline at this temperature is calculated to be 0·9004, and that of water 0·9094. The molecular volumes, therefore, are as 5·22 to 1, and the ratio of radii 1·73.

Phenol.—At the ordinary temperature phenol is a crystalline solid melting at 42·7°, and is only partly soluble in water; at 68·5° and higher temperatures it is miscible in all proportions. Rothmund (*loc. cit.*) found that the phenol layer at 20° contained 72·2 per cent. of phenol, as required by the formula $C_6H_6O,2H_2O$. The relative molecular volumes, referred to the gaseous state, are as 4·92 to 1, with a corresponding ratio of radii 1·70, a value suffi-

iently close to the theoretical to deduce a complexity similar to hat of water.

Disulphide.—Carbon disulphide is practically insoluble in water, and only partly miscible with methyl alcohol; with the higher alcohols, however, it is miscible in all proportions. The radius of its molecular sphere compared with that of water as unity would be expected to lie between 1·62 and 2·41, and to approximate more to the higher figure.

Mixtures of Carbon Disulphide with Ethyl Alcohol and with n-Propyl Alcohol at 15·5° (Holmes, T., 1906, **89**, 1784).

Equimolecular Volumes (gaseous). $\left.\begin{array}{l}100CS_2 : 96{\cdot}8C_2H_6O.\\ 100CS_2 : 124{\cdot}2C_3H_8O.\end{array}\right\}$

(i). Molecular mixture.		(ii). Expansion in volume when the volume of carbon disulphide is constant at 100 volumes in its mixtures with		(iii) (ΔCS_2). Difference between the proportions by volume of carbon disulphide in the initial and final volumes when mixed with	
CS_2.	$C_nH_{2n+1}OH$.	ethyl alcohol.	*n*-propyl alcohol.	ethyl alcohol.	*n*-propyl alcohol.
8	1	+0·37	+0·41	0·29	0·31
6	1	+0·45	+0·50	0·33	0·34
4	1	+0·59	+0·66	0·38	0·38
3	1	+0·72	+0·78	0·41	0·39
2	1	+0·92	+0·99	0·41	0·37
1	1	+1·45	+1·44	0·37	0·28

Allowing for displacement of the point of maximum difference due to differences in radii, these results are most consistent with a quadruple complexity of carbon disulphide as compared with the alcohols. Referred to the liquid state, equimolecular volumes of carbon disulphide and *n*-propyl alcohol would then be

$$100(CS_2)_4 : 31{\cdot}0C_3H_8O,$$

and ΔCS_2 removed to the mixture $[CS_2]_4,1\frac{1}{4}C_3H_8O$, as in the case of aqueous ethyl alcohol mixtures, in which the equimolecular volumes are the same (p. 2165). The ratio of radii is therefore 1·5, and the liquids are mutually miscible.

Similarly, in the ethyl alcohol mixtures the molecular volumes (liquid) are $100(CS_2)_4 : 24{\cdot}2C_2H_6O$, with a corresponding ratio of radii 1·61, and taking into consideration the relatively small volume change involved, the results are in agreement with the further displacement of the point of maximum difference, and also with the fact that below −14·4° these liquids have only a limited miscibility (Guthrie, *Phil. Mag.*, 1884, [v], **18**, 503).

Compared with the radius of the water molecule, and accepting

quadruple complexity, that of carbon disulphide is 2·37, which compares favourably with the theoretical value (2·41) for liquids insoluble in water. Further evidence is afforded by mixtures of carbon disulphide with methyl alcohol. The critical temperature for complete miscibility of the mixture $(CS_2)_4(CH_4O)_2$, representing one molecule of carbon disulphide and two molecules of methyl alcohol in the liquid state, is 40° (Rothmund, *loc. cit.*). The relative densities of the liquids at this temperature are 1·2318 and 0·7[illegible] respectively. The molecular volumes are therefore as 5·96 : 1, with a corresponding ratio of radii 1·81.

It will be noticed that the mixing of carbon disulphide with the alcohols results in a final volume which is greater than the sum of the initial volumes, and a ratio of radii is obtained at the critical point of solution, which is greater than those observed when contraction in volume occurs.

Chloroform and Benzene.—Chloroform, like ethyl ether, is only partly miscible with water, and to a much less extent. It is miscible, however, in all proportions with methyl alcohol and its homologues. Assuming similar complexity, its molecular volume at 20°, compared with that of water, would be 4·44, and the ratio of radii 1·64. According to the present theory, this is an impossible value for a liquid so sparingly soluble in water, and if molecular volume in the liquid state be represented by the quotient of molecular weight referred to the gaseous state by density, or a simple multiple of this quantity, the molecular volume of chloroform must be at least 8·89, and greater therefore than that of ethyl ether.

On similar grounds the value 4·92 calculated for the molecular volume of benzene (referred to the gaseous state) is also highly improbable.

The following volume changes are calculated from densities of chloroform–ethyl ether mixtures at 0° (Thorpe and Rodger, T., 1897, **71**, 360) and of benzene–ethyl ether mixtures at 25° (Linebarger, *Amer. Chem. J.*, 1896, **18**, 429).

Chloroform–Ether Mixtures.

Equimolecular Volumes (gaseous). $100CHCl_3 : 128·60C_4H_{10}O$.

(i).	(ii).	(iii) ($\Delta CHCl_3$).
$4CHCl_3,C_4H_{10}O$	−0·95	0·55
$3CHCl_3,C_4H_{10}O$	−1·22	0·60
$2CHCl_3,C_4H_{10}O$	−1·66	0·62
$CHCl_3,C_4H_{10}O$	2·85	0·55
$CHCl_3,2C_4H_{10}O$	−4·50	0·36

Benzene–Ether Mixtures.

Equimolecular Volumes (gaseous). $100C_6H_6 : 116{\cdot}92C_4H_{10}O$.

(i).	(ii).	(iii) (ΔC_6H_6).
$4C_6H_6,C_4H_{10}O$	$-0{\cdot}60$	$0{\cdot}36$
$3C_6H_6,C_4H_{10}O$	$0{\cdot}75$	$0{\cdot}39$
$2C_6H_6,C_4H_{10}O$	$-1{\cdot}01$	$0{\cdot}42$
$C_6H_6,C_4H_{10}O$	$-1{\cdot}38$	$0{\cdot}30$
$C_6H_6,2C_4H_{10}O$	$-1{\cdot}88$	$0{\cdot}17$

From these results the complexity of ethyl ether appears to be one-half of that of chloroform or benzene. It has already been shown that carbon disulphide has a quadruple complexity compared with that of ethyl ether, and the following mixtures of carbon disulphide with benzene serve to confirm the inference that these latter liquids are complexed in the proportion of two to one respectively.

Carbon Disulphide and Benzene (Brown, T., 1881, **39**, 202).

Equimolecular Volumes (gaseous). $100CS_2 : 147{\cdot}6C_6H_6$.

(i).	(ii).	(iii) (ΔCS_2).
$8CS_2,C_6H_6$	$+0{\cdot}46$	$0{\cdot}33$
$4CS_2,C_6H_6$	$+0{\cdot}76$	$0{\cdot}40$
$2CS_2,C_6H_6$	$+1{\cdot}29$	$0{\cdot}43$
CS_2,C_6H_6	$+2{\cdot}08$	$0{\cdot}34$
$CS_2,2C_6H_6$	$+2{\cdot}54$	$0{\cdot}26$

The ratios of the radii of chloroform and benzene molecules compared with that of water at 20° are, therefore, 2·07 and 2·14 respectively, values which are in agreement with their known solubilities.

n-Hexane.—It is probable that every liquid when mixed with some other suitable liquid will give volume-changes sufficient in amount to determine its relative complexity. Without this check, however, speculations based on solubility relations alone must at present be deemed unsatisfactory. It might be deduced, for instance, that the homologous series of liquid paraffins was doubly complexed as compared with the alcohols (1) from their insolubility in water, and (2) from the fact that the critical temperatures for complete miscibility of mixtures of carbon disulphide with methyl alcohol, and of *n*-hexane with methyl alcohol are almost the same, namely, 40·5° and 42·5° respectively (Rothmund). Carbon disulphide and *n*-hexane should have approximately the same molecular volumes.

The molecular volume of carbon disulphide at 15° is 13·30, and that of *n*-hexane, calculated from its molecular weight (gaseous) and density, is 7·19 when compared with that of water. This figure

is inconsistent with its known insolubility in water. If, however, we double the complexity, we get a molecular volume of 14·3, which approximates so closely to that of carbon disulphide that the above deduction regarding complexity would appear to be valid. The radius of the molecular sphere of *n*-hexane would thus be 2·43, which agrees with theoretical requirements for insolubility in water.

Methyl Iodide.—The complexity of methyl iodide has already been compared with the complexities of ethyl alcohol, *n*-propyl alcohol, acetone, and ethyl acetate (T., 1909, **95**, 1919). In each case the molecular volume ascertained from the curve of volume-change agrees with that required for relative solubility.

Ethyl Tartrate.—From the results of viscosity experiments it is usually assumed that the molecules of viscous liquids are highly complexed, and that the effect of solution is to break down these molecular aggregates to a simpler form. It is probable, however, that molecular complexity is not the determining factor in respect of the viscosities of liquids or of mixtures of liquids. If it be granted that a pure liquid is a collection of like spherical molecules, and the so-called molecular volume consists of an inner nucleus of great density, together with an outer sphere of influence which may differ in different liquids, an explanation of relative viscosity is to be sought rather in a comparison of the dimensions of these outer envelopes. Of these latter we have as yet little knowledge, except that liquids of great molecular volume, such as the paraffins, carbon disulphide, benzene, etc., are in general less viscous than pyridine, aniline, and the lower alcohols, of which the respective molecular volumes are less in proportion (see table, p. 2164). There appears, therefore, to be no a priori reason why a viscous liquid should be highly complexed, and, in fact, from the point of view of the present theory, the inference is in the opposite direction, namely, that viscous liquids have small molecular volumes, and by reason of their greater number in a given space, offer proportionately greater frictional surfaces in contact with each other.

The ethyl tartrate used in this investigation was prepared by dissolving tartaric acid in ethyl alcohol, and saturating the mixture with hydrochloric acid gas at a moderately low temperature. After remaining for some days the acid and excess of alcohol were removed, and the residue mixed with from four to five times its volume of pure ethyl alcohol, and again saturated with the gas. The ethyl tartrate was finally fractionated three times at pressures varying from 200 to 500 mm. The density of the sample was found to be 1·2099 at 15°/4°, and the observed rotation in a 100 mm. tube +8·65, or $[\alpha]_D^{15}$ +7·15°.

Ethyl tartrate is miscible with water and the lower alcohols in

proportions; the radius of its molecular sphere should be eater, therefore, than that of water, but not exceed the value 1·62. Much experimental work has been done by Patterson in conxion with changes of volume and rotation in ethyl tartrate ixtures (T., 1902, **81**, 1138 *et seq.*). In some of these mixtures, in hich the volume-changes were appreciable, the highest concentraon of ethyl tartrate was far removed from equimolecular proporons, and it was impossible, therefore, to construct the most imporant portion of the curves of volume-change. In the following ixtures of ethyl tartrate with water the densities were determined a bottle pyknometer of about 70 c.c. capacity, weights being educed to vacuum.

Percentage by weight of ethyl tartrate.	Density of mixture at 15°/4°.	When the volume of ethyl tartrate is constant at 100 volumes. Volume of water.	Contraction in volume.
95·748	1·20568	5·377	0·571
88·392	1·19535	15·902	1·393
85·063	1·18977	21·264	1·715
80·610	1·18183	29·128	2·128
74·803	1·17110	40·755	2·677
73·811	1·16910	42·965	2·757
69·700	1·16086	52·643	3·110
65·147	1·15151	64·786	3·503
57·552	1·13526	89·316	4·137
49·019	1·11664	125·941	4·902
40·653	1·09730	176·561	5·534
30·781	1·07384	272·316	6·274
30·174	1·07240	280·223	6·327
24·024	1·05736	382·969	6·676
20·417	1·04855	472·016	6·868
13·853	1·03239	753·064	7·067
11·314	1·02615	949·212	7·101

These volume-changes were plotted, and the following values obtained by interpolation:

Equimolecular Volumes (gaseous). $100C_8H_{14}O_6 : 10·58H_2O$.

(i).	(ii).	(iii) ($\Delta C_8H_{14}O_6$).
$C_8H_{14}O_6,H_2O$	−1·02	0·842
$C_8H_{14}O_6,2H_2O$	−1·71	1·181
$C_8H_{14}O_6,3H_2O$	−2·26	1·325
$C_8H_{14}O_6,4H_2O$	−2·74	1·379
$C_8H_{14}O_6,5H_2O$	−3·12	1·362
$C_8H_{14}O_6,6H_2O$	−3·48	1·330
$C_8H_{14}O_6,8H_2O$	−4·02	1·205
$C_8H_{14}O_6,12H_2O$	−4·91	0·971

The figures in column iii indicate that the complexity of ethyl tartrate is one-fourth of that of water, and if $C_8H_{14}O_6$ be taken as representing the molecular formula of ethyl tartrate in the liquid state, that of water must be $(H_2O)_4$. In these circumstances the molecular volume of ethyl tartrate compared with that of water is 2·36, and the ratio of radii 1·33. This value approximates closely to that already determined for methyl alcohol, and although these liquids would appear to have nothing in common in respect of

general properties or chemical constitution, still, if the basis of the theory is correct their relative solubilities should be comparable. Ethyl tartrate was found to be almost insoluble in the higher paraffins, and like methyl alcohol miscible only partly with carbon disulphide.

A mixture of carbon disulphide and ethyl tartrate was prepared in the molecular proportion $(CS_2)_4\frac{1}{2}(C_8H_{14}O_6)$—corresponding with one molecule of carbon disulphide and two molecules of ethyl tartrate in the liquid state. This mixture contained 8·1868 grams of ethyl tartrate and 24·1964 grams of carbon disulphide. The tube containing the mixture was sealed, and the temperature gradually raised in a water-bath. At temperatures below 35·9° the liquids were mutually miscible, but at 36·0° a cloudiness appeared in the *lower* part of the tube and spread rapidly through the mass of liquid, resulting in a separation into layers. The critical temperature of the corresponding mixture of carbon disulphide with methyl alcohol is 40° (p. 2156).

The density of carbon disulphide at 36°/4° is 1·2380, and that of ethyl tartrate 1·1890. Referred to the gaseous state the molecular volumes would be 61·50 and 173·35 respectively. Taking, however, the molecular complexities as determined above for the liquid state, namely, $(CS_2)_4$ and $\frac{1}{4}(C_8H_{14}O_6)$, the relative molecular volumes are 246·00 and 43·34, or as 5·68 to 1, with a ratio of radii 1·78. The ratio obtained for carbon disulphide–methyl alcohol was 1·81. These figures serve, therefore, to confirm the complexity of ethyl tartrate deduced from volume-change considerations.

Glycerol.—At the ordinary temperature glycerol is miscible in all proportions with water, methyl, ethyl, propyl, and butyl alcohols, but not with ethyl ether or the amyl alcohols. Its molecular sphere should approximate closely to that of water. Referred to the gaseous state, the molecular volume at 15° is 4·04 times that of water; solubility requirements would necessitate, therefore, a complexity for glycerol similar to that found for ethyl tartrate.

A sample of Kahlbaum's glycerol was fractionated in a vacuum, and the following mixtures made with ethyl tartrate:

Density of ethyl tartrate at 15°/4° = 1·20990.
Density of glycerol at 15°/4° = 1·26396.

Percentage by weight of ethyl tartrate.	Density of mixture at 15°/4°.	When the volume of ethyl tartrate is constant at 100 volumes. Volume of glycerol.	Contraction in volume.
86·833	1·22034	14·515	0·337
77·577	1·22674	27·667	0·534
68·038	1·23262	44·968	0·700
60·224	1·23693	63·222	0·804
54·263	1·24028	80·682	0·909
47·663	1·24376	105·109	1·015
42·513	1·24636	129·441	1·098
37·676	1·24869	158·345	1·170

From these figures the following values for molecular mixtures were interpolated:

Equimolecular Volumes (gaseous). $100C_8H_{14}O_6 : 42{\cdot}76C_3H_8O_3$.

(i).	(ii).	(iii) ($\Delta C_8H_{14}O_6$).
$3C_8H_{14}O_6,C_3H_8O_3$	$-0{\cdot}27$	$0{\cdot}22$
$2C_8H_{14}O_6,C_3H_8O_3$	$-0{\cdot}46$	$0{\cdot}31$
$C_8H_{14}O_6,C_3H_8O_3$	$-0{\cdot}69$	$0{\cdot}34$
$C_8H_{14}O_6,1\frac{1}{2}C_3H_8O_3$	$-0{\cdot}84$	$0{\cdot}31$
$C_8H_{14}O_6,2C_3H_8O_3$	$0{\cdot}94$	$0{\cdot}27$
$C_8H_{14}O_6,3C_3H_8O_3$	$-1{\cdot}10$	$0{\cdot}21$

These results are consistent with similar complexity, and the volume occupied by the glycerol molecule is practically identical with that of water. It is probable, therefore, that the viscous nature of both ethyl tartrate and glycerol may be ascribed to their small molecular volumes as compared with molecular weights in the liquid state, and the greater frictional surfaces exposed in the nestling together of the molecules.

The following table gives the radial ratios of the molecular spheres of liquids, which, on admixture at the stated critical temperatures of solution, are on the immediate border line between complete and partial miscibility:

Mixture.	Critical temperature of solution of the molecular mixture. M_{2m}.	Ratio of molecular radii at the critical temperature.
Nicotine and water	76°	1·65
Phenol and water	20	1·70
*iso*Butyric acid and water	7·5	1·72
Aniline and water	158	1·73
*iso*Butyl alcohol and water	113	1·75
Carbon disulphide and ethyl tartrate......	36	1·78
" " methyl alcohol ...	40	1·81

It will be noticed that the above ratios are somewhat greater than the theoretical (1·62). Nicotine and water give the nearest approach to this value, and they also give the greatest contractions in volume on admixture. In the other mixtures the ratios increase as the degree of contraction decreases, and reach the highest values when expansion in volume occurs. Since the mechanical close-packing of spheres must result necessarily in contraction in volume—greater, in fact, at the critical temperature than any hitherto observed—it is to be inferred that in true solution the effect of molecule on molecule is one of repulsion rather than of attraction, just as it is in a pure liquid. It has been shown in previous communications that volumetric changes resulting from the mixing of liquids can be represented, within a near approach to accuracy, by a calculable physical curve conditioned by the resultant of forces inherent in the molecules, whether contraction or expansion in volume occurs, whereas the corresponding changes obtained in mixtures in which chemical change is known to occur are to be

attributed to the physical nature and quantity of the new compounds formed, and lie on straight lines (T., 1909, 95, 1313). When, therefore, contraction occurs in solution, it is due to the fact that the change in volume resulting from close-packing is greater in magnitude than that due to the normal forces of repulsion.

Contraction in volume is usually accompanied by evolution of heat, and expansion in volume by absorption of heat. Binary mixtures are known, which afford both evolution and absorption of heat at different concentrations, as, for instance, chloroform and ethyl alcohol (Bussy and Buignet, *Ann. Chim. Phys.*, 1865, [iv], 4, 5), but there is no record of contractions and expansions in volume occurring in the same circumstances. As such behaviour was to be inferred from the present theory, a diligent search was made into the data already available, and many additional mixtures were examined with a view to obtaining information in this direction. It seemed probable that these peculiarities would occur only when the volume-changes were small, and preference was given more particularly to mixtures in which the density of one constituent was much greater than that of the other. Chloroform was mixed with methyl alcohol and also with ethyl alcohol, but contractions in volume alone were obtained. Mixtures of methyl iodide with methyl alcohol and *n*-amyl alcohol gave relatively large expansions at all concentrations. Methyl iodide mixed with ethyl ether afforded small contractions, and with chloroform small but appreciable expansions in volume. The curves of volume-change given by each pair of liquids were continuous, and had the usual character of physical curves. Mixtures of chloroform with acetone and with *n*-amyl alcohol gave the following results. The relative densities of these liquids and of their respective mixtures were determined at 25° in fine capillary pyknometers of 25 c.c. capacity, using a mercury-toluene thermostat.

Density of chloroform at 25°/25° = 1·48434.
Density of *n*-amyl alcohol at 25°/25° = 0·80915.
Density of acetone at 25°/25° = 0·78763.

Mixtures of Chloroform with n-*Amyl Alcohol.*

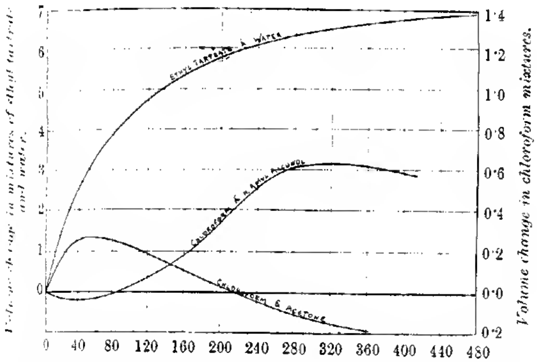
Weights in vacuum.		Density of mixture at 25°/25°.	When the volume of chloroform is constant at 100 volumes.	
Chloroform.	*n*-Amyl alcohol.		Volume of *n*-amyl alcohol.	Change in volume.
33·8719	4·2255	1·3581	22·89	+0·043
28·8802	6·9824	1·2765	44·35	−0·044
24·8772	9·0977	1·2132	67·08	+0·018
17·8526	12·9484	1·0993	133·00	−0·102
11·1636	16·6524	0·9915	273·60	−0·606
8·0171	18·1034	0·9415	414·30	−0·572

Mixtures of Chloroform with Acetone.

Weights in vacuum.		Density of mixture at 25°/25°.	When the volume of chloroform is constant at 100 volumes.	
Chloroform.	Acetone.		Volume of acetone.	Change in volume.
37·8495	2·2067	1·4165	10·99	−0·114
34·[illegible]	4·0230	1·3594	22·26	−0·196
28·[illegible]21	6·9097	1·2700	45·08	−0·270
21·[illegible]	10·4952	1·1532	91·23	−0·239
14·[illegible]	14·2312	1·0327	184·40	−0·053
9·[illegible]	17·4783	0·9373	361·07	+0·190

The volume-changes in these mixtures lie on sinuous but regular curves, showing both contractions and expansions in volume at

FIG. 3.



The base line represents volumes of water mixed with 100 volumes of ethyl tartrate, and volumes of n-amyl alcohol and of acetone mixed with 100 volumes of chloroform.

different concentrations (Fig. 3). It is difficult to see how these are to be explained, even by the elastic theory of ionic dissociation, or by any theory not acknowledging electrical affinities.

In the following table the liquids are ranged in the order of their molecular volumes as deduced from their relative complexities in the liquid state. The position of a liquid in this table decides its degree of miscibility with other liquids. Liquids adjacent to each other are miscible in all proportions, but when the ratio of the radii of the molecular spheres of any two liquids approximates to 1·7 there results a limited miscibility which becomes less in proportion to the further increase in this ratio.

Table of Molecular Complexities.

Liquid.	Temperature.	Complexity in the liquid state. Water = $(H_2O)_4$.	Molecular volumes compared with that of water as unity at the same temperature. Referred to the gaseous state.	Referred to the liquid state.	Molecular radius compared with that of water
Glycerol	15°	$C_3H_8O_3$	4·04	1·01	1·00
Formic acid	20	$(CH_2O_2)_4$	2·09	2·09	1·28
Methyl alcohol	15·5	$(CH_4O)_4$	2·23	2·23	1·31
Ethyl tartrate	15	$C_8H_{14}O_6$	9·45	2·36	1·33
Acetic acid	15	$(C_2H_4O_2)_4$	3·17	3·17	1·47
Ethyl alcohol	15·5	$(C_2H_6O)_4$	3·22	3·22	1·48
Propionic acid	25	$(C_3H_6O_2)_4$	4·06	4·06	1·60
Acetone	20	$(C_3H_6O)_4$	4·06	4·06	1·60
n-Propyl alcohol	25	$(C_3H_8O)_4$	4·16	4·16	1·60
Pyridine	15·5	$(C_5H_5N)_4$	4·44	4·44	1·64
Nicotine	20	$(C_{10}H_{14}N_2)_2$	8·92	4·46	1·65
Phenol	21	$(C_6H_6O)_4$	4·92	4·92	1·70
Aniline	25	$(C_6H_7N)_4$	5·06	5·06	1·72
n-Butyl alcohol	20	$(C_4H_{10}O)_4$	5·07	5·07	1·72
n-Butyric acid	25	$(C_4H_8O_2)_4$	5·08	5·08	1·72
*iso*Butyl alcohol	20	$(C_4H_{10}O)_4$	5·12	5·12	1·72
*iso*Butyric acid	20	$(C_4H_8O_2)_4$	5·13	5·13	1·72
Ethyl acetate	25	$(C_4H_8O_2)_4$	5·47	5·47	1·76
Ethyl ether	25	$(C_4H_{10}O)_4$	5·80	5·80	1·80
n-Amyl alcohol	20	$(C_5H_{12}O)_4$	5·98	5·98	1·82
Methyl iodide	25	$(CH_3I)_8$	3·49	6·98	1·91
Chloroform	20	$(CHCl_3)_8$	4·44	8·89	2·07
Ethyl iodide	20	$(C_2H_5I)_8$	4·48	8·97	2·08
Benzene	20	$(C_6H_6)_8$	4·91	9·83	2·14
Carbon disulphide	15·5	$(CS_2)_{16}$	3·32	13·30	2·37
n-Hexane	17	$(C_6H_{14})_8$	7·20	14·40	2·43
n-Heptane	14·9	$(C_7H_{16})_8$	8·06	16·13	2·53

Much additional information is available in connexion with many of these liquids, but it only serves to confirm the conclusions already arrived at. The experimental results do not depart materially from theoretical requirements, but each helps to confirm its fellows, and no exception has been found hitherto. There is little doubt, therefore, that the intermiscibility of liquids is a function of molecular volume, and being independent of chemical constitution, offers a means of ascertaining the molecular weights of liquids comparable perhaps with those based on Avogadro's hypothesis for the gaseous state.

Although it seems improbable in view of the preceding results, the question arises as to whether the complexity of a liquid is influenced by change of temperature. The volume ratio of the molecular spheres in a binary mixture certainly varies but little with temperature, and is, in fact, proportional to differences in the expansion coefficients of the liquids. Mixtures of ethyl alcohol with water, of which the densities at different temperatures are

...own more accurately than those of most liquid mixtures, afford ...e following values (calculated from Mendeléev's data, *Ann. Phys. Chem.*, 1869, [ii], **138**, 103, 230):

Equimolecular Volumes at 0° (gaseous). $100C_2H_6O : 31·55H_2O$.
...uimolecular Volumes at 15·5° (gaseous). $100C_2H_6O : 31·06H_2O$.
...uimolecular Volumes at 30° (gaseous). $100C_2H_6O : 30·68H_2O$.

	(ii).			(iii) (ΔC_2H_6O).		
(i).	0°.	15·5°.	30°.	0°.	15·5°.	30°.
$2C_2H_6O,H_2O$	2·59	2·41	2·29	1·98	1·85	1·76
$1\frac{1}{2}C_2H_6O,H_2O$ ...	3·12	2·91	2·77	2·19	2·05	1·95
C_2H_6O,H_2O	4·07	3·79	3·58	2·43	2·27	2·16
$C_2H_6O,1\frac{1}{4}H_2O$ ...	4·71	4·34	4·10	2·51	2·33	2·21
$C_2H_6O,1\frac{1}{2}H_2O$ ...	5·28	4·84	4·55	2·51	2·32	2·20
$C_2H_6O,1\frac{3}{4}H_2O$ ...	5·78	5·28	4·97	2·49	2·30	2·17
$C_2H_6O,2H_2O$	6·25	5·69	5·33	2·44	2·21	2·12

The degree of contraction varies to some extent with tempera...re (column ii), but the point of maximum difference between the ...roportion of ethyl alcohol in the initial and final volumes suffers ...ttle change (column iii, ΔC_2H_6O); in other words, the relative ...mplexity of ethyl alcohol and water is constant throughout this ...nge.

Similar results are given by aqueous mixtures of acetic acid ...d pyridine at different temperatures.

Correlation of Change in Volume in Mixtures of Ethyl Alcohol and Water with Specific Refraction.

One of the most important physical constants of a liquid is its ...dex of refraction, and just as the volume of a mixture of liquids ...most invariably differs from the sum of the initial volumes, so ...so the corresponding index of refraction of the mixture is not ...dditive. The index of refraction (n_D) of ethyl alcohol, for ...stance, is 1·36316 at 15·5°, and that of water 1·33336, but ...ixtures of the two give refractions far removed from the theo...retical, and a mixture containing 79·2 per cent. by weight, or 8... per cent. by volume of alcohol has a refractive index greater ...ven than that of either constituent, namely, 1·36661, and this is ...maximum for these liquids.

In the following table the differences in refraction from the ...heoretical are correlated with volume-changes at the several con...centrations. Columns i, ii, and iii have the same significance as in ...revious tables. Column ii*a* now gives the increase in the refractive ...ndex from the theoretical, when n_D C_2H_6O is 1·36316. Column iii*a* ...imilarly refers to differences (Δ) between the proportion of the ...efractive index due to alcohol in the theoretical and observed

refractions of the mixture. Columns iv and iv*a* refer to change in volume and refraction when calculated as a percentage on the initial volumes and initial refractions respectively, and column v gives the refractive index of the mixture at 15·5°, as determined in this laboratory by means of the Zeiss immersion refractometer.

Equimolecular Volumes (gaseous). $100C_2H_6O : 31{\cdot}06H_2O$.

$n_D C_2H_6O = 1{\cdot}36316$: $n_D H_2O = 1{\cdot}33336$.

(i).	(ii).	(ii*a*).	(iii). (ΔC_2H_6O).	(iii*a*). (ΔRefraction).	(iv).	(iv*a*).	v.
$4C_2H_6O,H_2O$ ...	−1·45	+0·00510	1·26	0·321	1·34	0·347	[illegible]
$2C_2H_6O,H_2O$ ...	2·41	0·00849	1·85	0·467	2·09	0·541	[illegible]
C_2H_6O,H_2O	3·79	0·01337	2·27	0·572	2·89	0·752	[illegible]
$C_2H_6O,1\frac{1}{4}H_2O$...	4·34	0·01538	2·33	0·588	3·13	0·815	[illegible]
$C_2H_6O,1\frac{1}{2}H_2O$...	4·84	0·01709	2·32	0·587	3·30	0·861	[illegible]
$C_2H_6O,1\frac{3}{4}H_2O$...	5·28	0·01858	2·30	0·576	3·42	0·890	[illegible]
$C_2H_6O,2H_2O$ ...	5·69	0·02001	2·24	0·563	3·51	0·913	[illegible]
$C_2H_6O,3H_2O$ ...	7·03	0·02159	1·95	0·489	3·64	0·944	[illegible]
$C_2H_6O,4H_2O$ ...	7·94	0·02731	1·64	0·405	3·54	0·904	[illegible]
$C_2H_6O,5H_2O$ ...	8·52	0·02939	1·35	0·337	3·34	0·846	[illegible]
$C_2H_6O,6H_2O$ ...	8·87	0·03053	1·11	0·279	3·09	0·793	[illegible]
$C_2H_6O,7H_2O$ ...	9·02	0·03095	0·92	0·231	2·84	0·726	[illegible]
$C_2H_6O,7\frac{1}{2}H_2O$ ..	9·09	0·03100	0·86	0·210	2·73	0·694	[illegible]
$C_2H_6O,8H_2O$ ...	9·08	0·03081	0·77	0·191	2·61	0·659	[illegible]
$C_2H_6O,9H_2O$ ...	9·07	0·03029	0·65	0·158	2·39	0·595	[illegible]
$C_2H_6O,10H_2O$...	8·99	0·02977	0·55	0·134	2·19	0·541	[illegible]
$C_2H_6O,12H_2O$...	8·78	0·02908	0·40	0·098	1·86	0·459	[illegible]
$C_2H_6O,20H_2O$...	7·88	0·02568	0·15	0·037	1·09	0·266	[illegible]
$C_2H_6O,101H_2O$...	6·79	0·02188	0·04	0·009	0·54	0·122	[illegible]

Whether we compare columns ii and ii*a*, iii and iii*a*, or iv and iv*a* the maximum differences in refraction occur at exactly the same concentrations as the maxima for volume-change, and the observed deviation in refraction from additive relations follows so closely the change in volume that deductions proceeding from the one set of phenomena are equally relevant to the other. These results give additional support, therefore, to the hypothesis that physical forces alone are operative in solution.

In conclusion, I desire to express my indebtedness to Mr. P. J. Sageman, of this laboratory, for the experimental data relating to the above chloroform mixtures, and also to Dr. J. J. Dobbie, M.A., F.R.S., for facilities afforded me in carrying on this investigation.

THE GOVERNMENT LABORATORY,
LONDON.

CCXXVIII.—*The Determination of Viscosity.*

By MALCOLM PERCIVAL APPLEBEY.

a recently-published criticism of viscosity investigations Bingham is vol., p. 959) has raised the question of the validity and uracy of the results obtained by the author and others with cometers of the Ostwald type. The importance to physical mists of a thorough and systematic examination of the labora- y methods of determining a property such as viscosity cannot ily be over-estimated. The work of Grüneisen (*Wiss. Abh. ys.-Tech. Reichs.*, 1905, **4**, 151), fully confirmed by the author's eriments (T., 1910, **97**, 2000), by those of Merton (T., 1910, , 2454), and recently by Washburn and Williams (*J. Amer. em. Soc.*, 1913, **25**, 737), who have effected a considerable im- vement in the method of standardising viscometers, leaves little m for doubt that the determination of relative viscosity can be rformed with great accuracy if sufficient care is taken in struction of the apparatus and in securing constancy of erimental conditions.

Relative and Absolute Viscosity.

Referring to the author's experiments, Bingham says (*loc. cit.*, 959): "It is a matter for particular regret when a research nned with the view toward the highest possible accuracy is ried out without the knowledge of conditions and correctious essary for making the results truly absolute." In the author's nion the question of the advisability of stating all viscosity data absolute values is of very small importance, and simply resolves elf into a matter of convenience. In the present state of know- ge it is actually much more convenient to state accurate relative ues as such, since the absolute viscosity of water cannot at sent be determined with the same accuracy as the relative cosity of a solution. The conversion of relative viscosities into solute therefore introduces into the data an uncertainty far ater than exists in the actual determinations. The following le will make this clear:

erage Variation from the Mean in Determinations of Viscosity by Different Viscometers.

(a) Relative Determinations.

Observer.	No. of viscometers used.	Range of viscosity (relative).	Variation. Per cent.
Grüneisen	3	0·920—3·272	0·028
Applebey	5	1·000—3·025	0·009*
Merton	2	0·835—1·000	0·008

* Not 0·1 as stated by Bingham.

(b) *Absolute Determinations.*

Observer.		Variation Per cent.
Bingham and White (*Zeitsch. physikal. Chem.*, 1912, **80**, 685)	(two arms of same viscometer)	[illegible]

Thus even on this basis, which does not sufficiently bring out the inaccuracy of the absolute determinations, an error is introduced eight times as large as the actual experimental error by converting the results into absolute values. If we compare the results of Bingham and White for the viscosity of water at the temperatures of the author's experiments with those of Thorpe and Rodger (*Phil. Trans.*, 1894, **185**, *A*, 397), it will be seen that the uncertainty is actually very much greater.

Viscosity of Water.

Temperature.	Thorpe and Rodger.	Bingham and White.	Difference Per cent.
0°	0·01778	0·01797	1·06
18	0·01062	0·01059	0·28
25	0·00891	0·008948	0·43

It should be stated, however, that the facts brought forward in this connexion are not in any sense advanced as a criticism of the work of Bingham and White. The determination of absolute viscosity is unfortunately rendered difficult by errors which can be avoided in the determination of relative viscosity, and it is not at all surprising that even careful work like that of Bingham and White should show errors and discrepancies far greater than those obtained with the simpler apparatus of Ostwald.

The Deviations from the Law of Poiseuille.

It is well known that in general the flow of liquids in capillary tubes is not strictly in accordance with Poiseuille's law:

$$\eta = \frac{\pi p r^4 t}{8 l V},$$

where η = coefficient of absolute viscosity,

p = mean pressure producing flow,

V = volume of liquid which flows through the capillary in time t,

r = radius,

and l = length of the capillary.

The inverse proportionality between pressure and time which Poiseuille's law demands, using the same liquid at the same temperature, is only found in the case when the pressures producing flow are small and the times of flow correspondingly large

As the time of flow diminishes, the product pt rises, and a correction factor has to be introduced into the Poiseuille expression to allow for this. Such corrections have been formulated by Neumann, Jacobsohn, Hagenbach, and Bingham and White on the assumption that the errors are due to the emergence of the liquid with a finite velocity from the end of the capillary.

On the other hand, Grüneisen has shown in a systematic study of the Ostwald viscometer that the deviations are not due to this cause, but to eddy formation at the points where there is rapid change in the character of the flow. With a well-made instrument the Poiseuille product $p \times t$ remains quite constant as t diminishes until a point of instability is reached, after which it rises rapidly, whilst the introduction of any correction of the kinetic energy type quite destroys the regularity of the results obtained. In these observations the author's work fully supports the conclusions of Grüneisen. The experiments of Merton and of Washburn and Williams (*loc. cit.*) are also completely in accord with Grüneisen's views. The last-named authors found, for a variation of the time of flow from 874·7 to 391·5 seconds, that the deviation from the mean value of $p \times t$ in no case exceeded 0·04 per cent.; if Bingham's contention were valid, a deviation of 3 per cent. would have been obtained.

It is found that the main factor in securing the efficiency of a viscometer is the character of the joins between the capillary and the reservoirs. For the preservation of the condition of stationary flow it is necessary that the joins should be even and without irregularity, and that the change of diameter should be gradual. The condition which necessarily prevails in Bingham and White's experiments, as in all absolute determinations, is extremely unfavourable to the maintenance of the correct type of flow, since the change of diameter is sudden, owing to the necessity of cutting off the capillary squarely so that its length can be measured. The flow in an absolute viscometer is probably of the type described by Bingham,* the liquid passing as a jet from the end of the capillary into the reservoir, and there expending its kinetic energy in eddies which do not resist the motion of the liquid still in the capillary to the same extent as in the case of Poiseuille motion. In an Ostwald viscometer, however, within the limits of its obedience to the law of Poiseuille, the type of flow is quite different, and eddying is entirely absent.

* The experiment quoted by Bingham, in which a long capillary was cut in pieces, is in many respects similar to Poiseuille's experiment with the tube BIV, which is considered by Grüneisen.

Constancy of Experimental Conditions.

Bingham objects to the slow flow viscometer that it is difficult to ensure constancy of conditions during the determinations. It is, of course, true that care must be exercised in the performance of accurate viscosity determinations as in any other accurate determinations. The difficulties referred to by Bingham are of three kinds:

(*a*) *Cleanliness.*—The vitiation of experiments by the intrusion of dust particles was, the author believes, a source of more trouble in his experiments than in those of earlier observers simply because the accuracy aimed at was higher. Very frequently experiments had to be discarded which showed in successive times of flow discrepancies which amounted only to 0·1 per cent., or even less. Such experiments would have been valid and unobjectionable if the conditions of experiment and the accuracy attainable had been of the order of those which prevail in the determination of absolute viscosity.

(*b*) *Constancy of Filling.*—This difficulty was specially tested for, and found to be of no account. The variation of pressure produced by the maximum variation in six fillings by a pipette was only 0·002 per cent. (*loc. cit.*, p. 2011). Washburn and Williams also arrive at 0·002 per cent. as the maximum error occasioned by this means. Bingham's suggestion of an error of 0·01 cm. in the head of liquid would mean an error of filling of 0·11 gram, which is far outside the average error of a properly used pipette.

(*c*) *Constancy of Temperature.*—With a Lowry spiral regulator actuating a post-office relay through which runs the current for a heating lamp, there is no difficulty in keeping a well-stirred bath constant to 0·01° for weeks at a time, and with care the variations may be actually reduced to as little as 0·002°. The following points which the author has found to be essential for good temperature regulation will perhaps be of use to other observers.

(1) The relay contacts and the platinum-mercury contact at the top of the regulator must be kept quite clean by preventing sparking at these points. An entirely satisfactory method is to join up a condenser made of two aluminium plates immersed in tap-water across each spark-gap. The condenser used in the lamp circuit only becomes efficient after some time, usually a few hours, but after that time no spark can be seen in a dark room with a voltage of 100.

(2) Sticking of platinum and mercury must be avoided by keeping the mercury surface moving. The best way to secure this is by attaching regulator and stirrer to the same stand and arrangement which keeps the mercury surface just trembling and

ensures rapid action. A regulator works best when it makes and breaks contact two or three times a second.

(3) It is advisable in using spiral regulators to cut a slit in the side of the cork which carries the upper contact so as to enable the pressure inside the regulator to be always equal to the external pressure. Spiral regulators respond quite considerably to differences of internal and external pressure, with the result that a regulator which is quite closed regulates at slightly different temperatures for different barometric pressures.

Gas regulation is not quite so efficient, but the variations can be quite easily kept down to 0·01°.

THE LEOLINE JENKINS LABORATORY,
JESUS COLLEGE, OXFORD.

CCXXIX.—*A Series of Mixtures of Nitro-compounds and Amines, which are Coloured in the Liquid State Only.*

By CHARLES KENNETH TINKLER.

SOME time ago in connexion with an investigation by the author into the cause of the colour of certain alkyl iodides of cyclic bases, the molecular weights of these substances, in diphenylamine solution, were determined by the cryoscopic method (T., 1909, 95, 921).

The view was then put forward that the colour of some of these substances was due to polymerisation. From this investigation followed the examination of certain other substances in diphenylamine solution.

It was found that certain nitro-compounds, when dissolved in diphenylamine, give strongly-coloured solutions, but that the colour disappeared completely on solidification; thus a mixture of *p*-chloronitrobenzene and diphenylamine, which is colourless at the ordinary temperature, assumes a reddish-yellow colour at somewhat below body temperature, and loses this colour entirely when cooled.*

Again, a mixture of *p*-nitrobenzaldehyde and diphenylamine shows a deep red colour at slightly above body temperature, returning to the colourless condition when the temperature falls.

* For the demonstration of this phenomenon of colour-change the mixture is conveniently contained in a thin layer between two test-tubes placed one inside the other.

A large number of other nitro-compounds, such as *o*- and *m*-chloronitrobenzene, *p*-bromo- and iodo-nitrobenzenes, *m*-nitrobenzaldehyde, *m*-nitrobenzonitrile, *p*-nitrotoluene, *m*- and *p*-nitrobenzoic acids, etc., also show the phenomenon to varying extents. Other amines, such as *p*-toluidine, tribenzylamine, or triphenylamine, may be substituted for the diphenylamine in some cases.

As is well known, mixtures of amines and nitro-compounds, such as trinitrobenzene and picryl chloride, often give rise to permanently coloured compounds (Hepp, *Annalen*, 1882, **215**, 344; Sudborough, T., 1901, **79**, 572; 1902, **81**, 507, etc.; Noelting and Somerhoff, *Ber.*, 1906, **39**, 76, and others), whilst other investigators have observed the production of coloured solutions by dissolving amines in tetranitromethane (Ostromisslensky, *Ber.*, 1910, **43**, 197; A. Werner, *Ber.*, 1909, **42**, 4324); thus diphenylamine and trinitrobenzene give a strongly-coloured compound, produced by the combination of one molecule of amine and two of nitro-compound. No change in colour is produced on cooling this substance.

It is of interest to note that an aromatic nitro-compound is not necessary for this phenomenon of colour change; thus on the addition of tetranitromethane to solid diphenylamine a very dark brown coloration is produced, which is entirely removed when the mixture is cooled in ice and salt. After repeating this last experiment several times a permanent green coloration is produced, probably owing to the decomposition of the nitro-compound. In the case of the mixture of *p*-chloronitrobenzene and diphenylamine, however, a tube filled with the mixture five years ago shows the phenomenon as well now as when first prepared.

The temperature necessary to produce the colour in any given mixture depends simply on the melting points of the constituents of the mixture, or rather, as will be shown later, on the eutectic temperature of the mixture, and whenever colour is produced, part at least of the mixture is in the liquid state. The phenomenon depends on a change of state rather than on a change of temperature.

The action of solvents on the mixtures under review leads to the production of colour in very concentrated solution, but the colour is easily removed on dilution; thus a concentrated solution of *o*-chloronitrobenzene and diphenylamine in benzene rapidly becomes colourless on dilution, more readily, however, on dilution with alcohol than with benzene. Again, on mixing dilute solutions of the nitro-compound and amine, no colour is produced. This is in agreement with the behaviour of some of the additive compounds of trinitrobenzene and amines which are decomposed by solvents (compare Sudborough, *loc. cit.*).

On attempting to precipitate the coloured substance by the [illegible]dition of water to a concentrated alcoholic solution of one of [illegible] mixtures, a red substance is produced, and at first sight it [illegible] appear that a compound of nitro-derivative and amine was [illegible]tained, which existed in the solid state. On closer investigation, [illegible]wever, it is found that the colour is due to the fact that the [illegible]xture is supercooled, as when the mixture is completely solidi[illegible] by agitation, the colour entirely disappears. A suitable [illegible]xture for the demonstration of this phenomenon is one of [illegible]phenylamine containing about one-third of its weight of *p*-nitro[illegible]nzaldehyde.

On subjecting some of these mixtures to fractional distillation [illegible] is found, as would be expected, that the constituent of lower [illegible]iling point is present in excess in the first portion of the distil[illegible]te, and that the phenomenon of colour change is shown to a [illegible]rying extent with each portion of the distillate.

Attempted Explanation of the Phenomenon.

In looking for an explanation of the phenomenon of colour [illegible]ange on heating and cooling, it has to be borne in mind that [illegible]strongly-coloured compounds of amines and nitro-derivatives, such as trinitrobenzene, previously referred to, are well known sub[illegible]stances, although, as will be shown later, no evidence of compound[illegible]formation has so far been obtained in the mixtures under review. Also, the presence of a nitro- and amino-group in the same molecule often gives rise to intense colorations, as, for example, in the nitroanilines.

Various formulæ have been suggested for the compounds of [illegible]ine and nitro-derivative where such compounds have been [illegible]lated, and, as in the case of the nitroanilines, a quinonoid [illegible]nstitution has been assigned to them by some investigators on [illegible]count of their colour.

A quinonoid constitution, however, does not appear to be neces[illegible]ary for the substances under review, since the aliphatic nitro[illegible]compound, tetranitromethane, may be used as the nitro-compound [illegible] the mixture. Similarly, an aromatic amine is not necessary [illegible]or the production of a colour with a nitro-compound. Many nitro[illegible]compounds, such as di- and tri-nitrobenzenes, give strongly-coloured [illegible]lutions in liquid ammonia, and a red additive compound of [illegible]ammonia and trinitrobenzene has previously been described (Korczyński, *Bull. Acad. Sci. Cracow*, 1908, 333).

Finally, tetranitromethane and liquid ammonia give an orange-yellow solution, which by its own evaporation produces a yellow solid, and A. Werner (*loc. cit.*) has previously observed that tetra[illegible]nitromethane and trimethylamine give a strongly-coloured solution.

In these cases, however, the possibility of the formation of the coloured modification of nitroform has to be taken into account.

The change from colourless to coloured and vice versa in these mixtures is doubtless due to some change in the configuration of the nitro-group, as in the case of nitrogen peroxide, N_2O_4, and nitrogen dioxide, NO_2; in fact, the production of a white solid, by the freezing of one of these coloured mixtures, shows a striking resemblance to the production of a white solid by freezing the coloured liquid nitrogen peroxide.

The colour-change is also doubtless connected with the residual affinity of the amine. For just as the strongly-coloured nitroanilines give colourless solutions in concentrated hydrochloric acid, so the substitution of bromine or chlorine for hydrogen in the diphenylamine disturbs the distribution of the residual affinity of the amine, and tetrachloro- and tetrabromo-diphenylamine do not give these colour reactions with nitro-compounds.

Baly, Tuck, and Marsden (T., 1910, **97**, 571) point out that in the case of certain nitro-compounds, such as nitroquinol dimethyl ether, α-nitronaphthalene, and 4-nitro-*o*-xylene, an increase in the residual affinity of the solvent causes a shift in the absorption band towards the red end of the spectrum. It is possible, therefore, that the phenomena observed when nitro-compounds are dissolved in diphenylamine is an extreme case of this process of colour intensification.

According to Hantzsch (*Ber.*, 1912, **45**, 85), it is necessary to distinguish between three kinds of nitro-group attached to carbon:

(1) The true nitro-group, $:C\cdot N\ll\begin{array}{l}O\\O\end{array}$ or $:C\cdot N<\begin{array}{c}O\\|\\O\end{array}$, present in nitro-compounds, such as nitromethane;

(2) the *aci*nitro-group, $:C:\underset{\overset{\|}{O}}{N}\cdot O\cdot M$ or $:C:N\cdot O\cdot OM$, present in the salts of nitro compounds;

and (3) the conjugated *aci*nitro-group, $\cdot C:\overset{-X\cdots}{\underset{\overset{\|}{O}}{N}}\cdot O\cdot M$ or $\cdot C:N\cdot O\cdot \overset{X}{O}\cdot M$, where the nitro-group is associated in the same molecule with an electronegative group X (NO_2, NOH, CO_2H, CN, etc.), to which it is united by subsidiary valency through the metal, alkyl radicle, or hydrogen directly attached to the nitro-group.

The absorption due to the first two types does not fall in the visible region of the spectrum, but the third type is characterised by strong absorption, which extends into the visible region of the spectrum.

It is possible that the colour in some of the mixtures under review might be due to a change in the configuration of the nitro-group similar to the formation of a conjugated *aci*nitro-group, but

this hypothesis would not explain the colours of mixtures containing tetranitromethane. In the case of this substance it is impossible to write an ordinary conjugated *aci*nitro-group, as none of the nitro-groups can be attached to carbon by a double bond.

The permanent colour production observed in solution with tetranitromethane and various substances having residual affinity, first noticed by Ostromisslensky and also by A. Werner (*loc. cit.*), is being investigated by Clarke, Macbeth, and Stewart by means of the spectrograph (P., 1913, **29**, 161). Since it is probable that the permanent colours produced in these cases are due to a cause similar to that which produces the transient colours in the mixtures referred to in the present paper, the question as to the cause of this colour will again be dealt with in a later communication. At present it appears possible that the attraction between the amine and the nitro-group causes a distribution of residual affinity in the latter, which approximates more or less to that in the dissociated form of nitrogen peroxide, $<^{O}_{O}$.

Physico-chemical Investigations of the Mixtures.

Various physico-chemical investigations have been undertaken in order to detect, if possible, the formation of a compound between the amine and nitro-derivative in these mixtures.

The first method tried was the determination of melting-point curves for the mixtures, which is the usual method for the detection of such combinations. In these mixtures, however, no evidence of any compound formation was obtained by this method. In the cases investigated all the curves obtained showed a eutectic, and were V shaped. No W-shaped curve was obtained.

In order to obtain a W-shaped curve it would appear to be necessary that the compound should separate in the solid state, but this is not the case in these mixtures, or they would remain coloured on cooling or precipitation from solution.

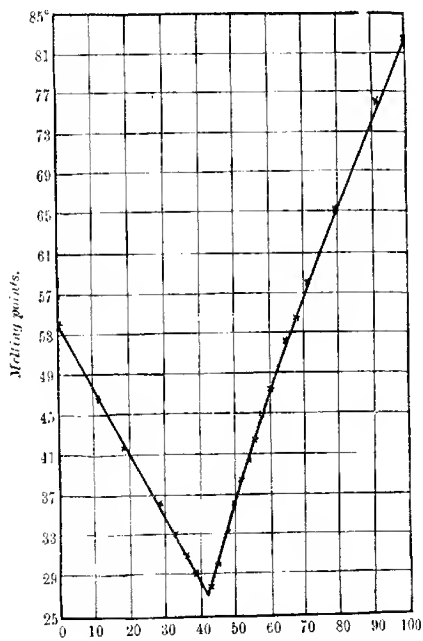
It was found in the course of these experiments that on heating up a given mixture, as soon as the temperature reaches the eutectic temperature the colour begins to develop, that is, the colour is dependent on the presence of liquid. It is also noticed that when a mixture is completely liquefied it has developed its maximum colour.

The melting-point curve for mixtures of *p*-chloronitrobenzene and diphenylamine is shown in Fig. 1. The eutectic temperature of the mixture is 27°, and the eutectic mixture contains 42·5 molecular percentage of the nitro-derivative. On heating the various mixtures of these two substances the colour commences to develop at 27°. If, however, a mixture contains a very large percentage

of the nitro-derivative, the colour begins to develop at a slightly lower temperature.

Spectroscopic investigation, which has been limited to dilute solutions of mixtures containing aromatic nitro-compounds, has so far failed to throw any light on the subject. No visible colour is produced by mixing dilute solutions of the constituents of a mixture, and the ultra-violet absorption produced by a certain

FIG. 1.



Molecular percentage of p-*chloronitrobenzene.*

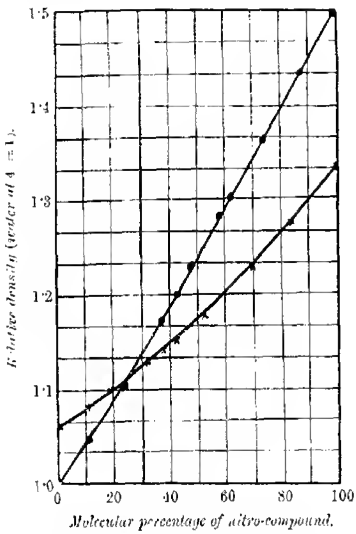
Melting-point curve of mixtures of diphenylamine and p-*chloronitrobenzene.*

thickness of layer is identical with that produced by layers half the thickness of the constituent solutions taken side by side, showing that in dilute solution the amine and nitro-compound are without action on one another.*

* Since this paper was written, it appears from some preliminary experiments that with very concentrated solutions it is possible to determine spectroscopically the proportions in which the substances exert maximum effect, as to colour production, on one another (compare Ostromisslensky, *Ber.*, 1911, **44**, 268).

A series of density determinations of the fused mixtures was undertaken, both in the case of one of these mixtures showing the phenomenon of colour change, and in the case of permanent compound formation. The diagram, Fig. 2, shows the results obtained. In both cases very little deviation from a straight line is observed. The determinations were carried out at 60° and 130° respectively. The method employed was that of weighing a sphere of known volume in the mixture kept at the required temperature by means of a thermostat.

Fig. 2.



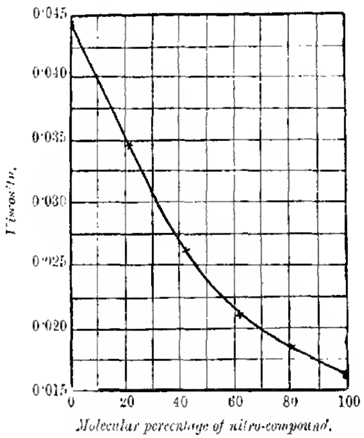
Relative densities of mixtures of:
I. *Diphenylamine and o-chloronitrobenzene at 60°* —×—×—
II. ,, ,, *trinitrobenzene at 130°* —·—·—

Experiments were carried out to ascertain if any rise of temperature occurred on mixing the fused constituents of the mixtures under review. In no case was a rise of more than 0·4° observed, even when 10 grams of one of the constituents were mixed with 5 grams of the other. This, however, does not afford evidence of non-compound formation, as in the case where a compound is formed in the solid state, for example, with diphenylamine and trinitrobenzene, on mixing 8 grams of the former with $2\frac{1}{2}$ grams of the latter, both at 138°, a rise of only 0·4° was observed.

Viscosity measurements were made on mixtures of o-chloronitrobenzene and diphenylamine, but as will be seen from the diagram, Fig. 3, no definite conclusion as to the formation of a compound can be drawn from this result.

It is possible that none of these methods is sufficiently accurate to detect the formation of a small amount of compound which might give rise to the colour. Other physico-chemical determinations remain to be carried out, but so far only from analogy to the compounds of amines and nitro-derivatives, which can be obtained in the solid state, can it be said that when in the coloured condition the mixtures under review contain compounds of the two constituents.

Fig. 3.



Viscosities in absolute units of mixtures of diphenylamine and o-chloronitrobenzene at 60°.

These compounds, if formed, must, however, be very unstable, since the cohesion of one or both of the constituents in the solid state is sufficient to overcome the molecular attraction of the one substance for the other. On the other hand, the presence of the amine in the fused state may be sufficient to cause the nitro-compound to assume a constitution, which gives rise to the colour, without any chemical combination taking place between the two substances.

The investigation is being extended to mixtures of nitro-derivatives and phenols and nitro-derivatives and hydrocarbons. As is well known, certain nitrophenols are coloured substances, and others give rise to coloured salts. Sudborough and Beard (T., 1911, 99,

have prepared a large series of coloured additive compounds of nitro-derivatives, such as trinitrobenzene, and certain phenols. Coloured compounds of nitro-derivatives and hydrocarbons are also, of course, well known.

Certain of the nitro-compounds mentioned in this paper, especially tetranitromethane, when mixed with phenols, such as thymol or a-naphthol, and with certain hydrocarbons, such as naphthalene, give strongly coloured mixtures, from which the colour is entirely removed by cooling in a freezing mixture. Similar phenomena are also shown by certain mixtures of ketones and diphenylamine; thus a mixture of anthraquinone and diphenylamine develops an intense coloration on heating, which is lost on solidification and precipitation from solution.

The investigation will therefore be extended to include these substances, and also to certain mixtures containing iodine compounds.

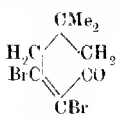
THE UNIVERSITY, EDGBASTON,
BIRMINGHAM.

CCXXX.—*Derivatives of* o-*Xylene. Part VI. 5-Bromo*-o-3-*xylenol.*

By ARTHUR WILLIAM CROSSLEY.

In 1903 (T., 83, 128) the present author, in conjunction with Le Sueur, showed that under certain conditions phosphorus pentabromide acted on dimethyldihydroresorcin to give a monobromoxylenol melting at 84°. At that time the only point definitely established about its constitution was that it gave tribromo-*o*-3-xylenol on treatment with bromine, and that it was therefore a monobromo-*o*-3-xylenol.

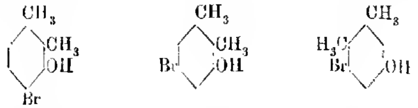
More recently this same bromoxylenol has been obtained by the action of (*a*) heat, (*b*) potassium hydroxide on dibromodimethylcyclohexenone (I), a substance the constitution of which has been



(I.)

definitely established (compare this vol., p. 989). There would therefore appear to be only two possibilities (II and III) for the

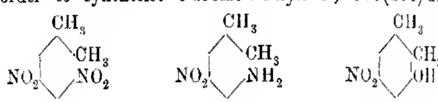
constitution of this bromoxylenol, if it is accepted that, during the rearrangement, the ketonic group of the hydroaromatic substance becomes phenolic, and one of the methyl groups wanders into position 2:



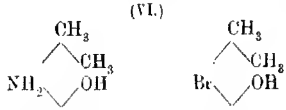
(II.) (III). (IV.)

Of these two formulæ the latter appears to be the more probable, because it has already been shown (compare this vol., p. 1297) that by the action of heat on dibromodimethyl*cyclo*hexenone (I.), 6-bromo-*o*-4-xylenol (IV) is formed; that is to say, it is the bromine atom in position 5 of dibromodimethyl*cyclo*hexenone which remains in the resulting bromoxylenol, and this is therefore in all probability the bromine atom which would be found in the bromoxylenol in question. The production of the two xylenols would arise from the wandering in the one case of a methyl group from position 1 to position 2, and in the second case of a methyl group from position 1 to position 6; otherwise the rearrangement would be of an entirely similar nature.

In order to synthesise 5-bromo-*o*-3-xylenol, 3:5(4:6)-dinitro-*o*-



(V.) (VI.) (VII.)



(VIII.) (IX.)

xylene (V) (T., 1909, **95**, 209) was converted into 5-nitro-*o*-3-xylidine (VI), as already described (T., 1911, **99**, 2351). In this substance the amino-group was replaced by hydroxyl, the resulting nitroxylenol (VII) reduced to 5-amino-*o*-3-xylenol (VIII), in which compound the amino-group was replaced by a bromine atom, giving rise to 5-bromo-*o*-3-xylenol (IX), which was found to melt at 81°, and to be identical with the substance obtained by the action of phosphorus pentabromide on dimethyldihydroresorcin.

Experimental.

5-Nitro-*o*-3-xylidine (T., 1911, **99**, 2351), in quantities of 5 grams at one time, was suspended in 70 c.c. of 40 per cent. sulphuric acid

and diazotised by the addition of the requisite amount of a 20 per cent. sodium nitrite solution, at first at the temperature of the laboratory and afterwards at 50—60°. The whole was then poured into 120 c.c. of 40 per cent. sulphuric acid and heated on a water-bath until gas was no longer evolved. On cooling the oily mass, which at first separated, solidified. It was extracted with ether, the ethereal solution washed with sodium hydroxide, the washings acidified and allowed to stand, when the solid which separated was purified by crystallisation from chloroform and then benzene:

0·2120 gave 15·8 c.c. N_2 (moist) at 19° and 755 mm. N = 8·51.
$C_8H_9O_3N$ requires N = 8·38 per cent.

5-*Nitro*-o-3-*xylenol*, of which the yield of purified material is about 65—70 per cent. of the theoretical, is insoluble in light petroleum (b. p. 40—60°), very soluble in the acid in alcohol, acetone, or ethyl acetate, and crystallises from either chloroform or benzene in radiating clusters of small, orange-yellow needles, melting at 109°.

5-Nitro-*o*-3-xylenol was reduced in quantities of 2 grams at one time by dissolving in 100 c.c. of absolute alcohol, heating on the water-bath, and adding a saturated solution of sodium hyposulphite (Grandmougin, *Ber.*, 1906, **39**, 2494). After the addition of water, the solution was made alkaline with ammonium hydroxide and the alcohol evaporated. It is essential to get rid of the last traces of alcohol, as otherwise the yield of material is very considerably diminished. The resulting solid was crystallised from benzene, and analysed:

0·1303 gave 12·0 c.c. N_2 (moist) at 20° and 760 mm. N = 10·53.
$C_8H_{11}ON$ requires N = 10·22 per cent.

5-*Amino*-o-3-*xylenol* is readily soluble in the cold in acetone, or ethyl acetate, readily soluble in alcohol or water on warming, and crystallises from chloroform or benzene, in which solvents it is not easily soluble, in aggregates of small, orange needles, melting at 179°. The yield is about 40 per cent. of the theoretical.

Two grams of 5-amino-*o*-3-xylenol dissolved in 20 c.c. of water and 6 grams of 40 per cent. hydrobromic acid were diazotised at 0° with the calculated quantity of a 20 per cent. solution of sodium nitrite, the whole poured into a solution of 1 gram of cuprous bromide in 5 c.c. of 40 per cent. hydrobromic acid, allowed to stand for one hour, and then steam distilled. The solid, which passed over with the steam, was purified by crystallisation from light petroleum (b. p. 40—60°) and the bromine determined:

0·1104 gave 0·1031 AgBr. Br = 39·73.
C_8H_9OBr requires Br = 39·80 per cent.

5-*Bromo-o-3-xylenol* is readily soluble in potassium hydroxide solution, alcohol, benzene, acetone, or chloroform, is insoluble in sodium carbonate solution, and crystallises from light petroleum (b. p. 40—60°) in radiating clusters of long, white, glistening needles, melting at 84°. The yield is only about 45—50 per cent. of the calculated on the aminoxylenol used, and undoubtedly the easiest method for the preparation of this bromoxylenol in large quantities is from hydroaromatic substances as will be described in a later communication.

The *benzoyl* derivative, prepared in the usual manner, is readily soluble in the cold in acetone, ethyl acetate, benzene, or chloroform, and crystallises from alcohol in colourless, transparent, rhombic plates, melting at 98°:

0·1188 gave 0·0743 AgBr. Br = 26·61.

$C_{15}H_{13}O_2Br$ requires Br = 26·23 per cent.

The o-*nitrobenzoyl* derivative, obtained in the ordinary way, is soluble in the cold in chloroform, ethyl acetate, acetone, or benzene, and crystallises from alcohol in radiating clusters of thin, glistening, transparent needles, melting at 128°:

0·2982 gave 10·6 c.c. N_2 (moist) at 20° and 759 mm. N = 4·06.

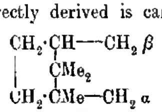
$C_{15}H_{12}O_4NBr$ requires N = 4·00 per cent.

RESEARCH LABORATORIES, PHARMACEUTICAL SOCIETY,
17, BLOOMSBURY SQUARE, W.C.

CCXXXI.—l-*Epicamphor* (l-β-*Camphor*).

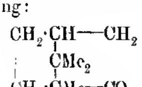
By JULIUS BREDT and WILLIAM HENRY PERKIN, jun.

THE hydrocarbon from which camphor and its many derivatives may be said to be directly derived is camphane (Aschan, *Ber.*,



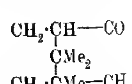
Camphane.

1900, **33**, 1009), and it is clear that this hydrocarbon must yield two different keto-derivatives by the substitution, on the one hand, of the α-, and on the other of the β-CH_2 group by CO, namely, the following:



Camphor or α-camphor.

and



Epicamphor or β-camphor.

It is well known that Bredt (*Ber.*, 1893, **26**, 3047; *Annalen*, 1896, **292**, 33) originally suggested that the first of these formulæ most probably represents the constitution of camphor, and the correctness of this view has been abundantly proved by the great mass of experimental evidence which has accumulated, especially during the last few years.

The other possible isomeride—*epicamphor*—must be a substance the importance of which, at all events from the chemical point of view, can hardly be less than that of camphor itself, and indeed the study of the reactions and decompositions of epicamphor might be expected to afford clues to the constitution and relationship of some of the more complex derivatives of camphor which can hardly be obtained, or at least not so readily, from the study of camphor itself.

It is indeed obvious that the study of epicamphor, and especially the careful comparison of the properties of its derivatives with those of the corresponding derivatives of camphor, is a problem so attractive that it is not surprising to find evidence that repeated efforts have been made from time to time by different investigators to devise some process for the preparation of epicamphor, but, until recently, without success. In 1900, Duden and Macintyre (*Annalen*, **313**, 59) attempted to solve the problem by starting with *iso*nitrosocamphor, which they first reduced to aminocamphor and then to aminoborneol:

$$C_8H_{14}<\begin{matrix}C{:}N{\cdot}OH\\|\\CO\end{matrix} \longrightarrow C_8H_{14}<\begin{matrix}CH{\cdot}NH_2\\|\\CO\end{matrix} \longrightarrow C_8H_{14}<\begin{matrix}CH{\cdot}NH_2\\|\\CH{\cdot}OH\end{matrix};$$

they proposed then to remove water from the latter substance in order to obtain *l*-aminobornylene, from which, by the action of nitrous acid, *l*-epicamphor should result:

$$C_8H_{14}<\begin{matrix}CH{\cdot}NH_2\\|\\CH{\cdot}OH\end{matrix} \longrightarrow C_8H_{14}<\begin{matrix}C{\cdot}NH_2\\||\\CH\end{matrix} \longrightarrow C_8H_{14}<\begin{matrix}CO\\|\\CH_2\end{matrix}.$$

It was, however, not found possible to remove water directly from aminoborneol, and this base was therefore treated with phosphorus pentachloride, when it yielded α-chloro-β-aminocamphane, a substance which might be expected to yield aminobornylene by the elimination of hydrogen chloride:

$$C_8H_{14}<\begin{matrix}CH{\cdot}NH_2\\|\\CHCl\end{matrix} \longrightarrow C_8H_{14}<\begin{matrix}C{\cdot}NH_2\\||\\CH\end{matrix}.$$

Elimination of hydrogen chloride did actually take place when the chloroamino-compound was distilled with aqueous sodium hydroxide, but the base (camphenamine) which was produced is not aminobornylene since, in place of epicamphor, it yields a substance having the properties of an unsaturated tertiary alcohol

(*iso*camphor) when it is treated with nitrous acid. It is therefore clear that intramolecular change must have taken place, probably during the elimination of hydrogen chloride from chloroamino-camphane.

At a somewhat later date (*Compt. rend.*, 1905, **141**, 697) Haller and Blanc attempted to obtain epicamphor by a process similar to that which they had employed with success in the case of camphor itself. When camphoric anhydride is reduced by sodium amalgam it yields α-campholide, and this reacts with potassium cyanide to form an additive product, which, on hydrolysis, is converted into homocamphoric acid, and camphor is obtained by the distillation of the calcium or lead salt of this acid:

$$C_8H_{14}<\begin{matrix}CO\\CO\end{matrix}>O \longrightarrow C_8H_{14}<\begin{matrix}CH_2\\CO\end{matrix}>O \longrightarrow C_8H_{14}<\begin{matrix}CH_2\cdot CN\\CO_2K\end{matrix}$$

$$C_8H_{14}<\begin{matrix}CH_2\cdot CO_2H\\CO_2H\end{matrix} \longrightarrow C_8H_{14}<\begin{matrix}CH_2\\|\\CO\end{matrix}.$$

Haller and Blanc now prepared β-campholide from methyl hydrogen camphorate by conversion into the acid chloride and subsequent reduction with sodium and alcohol:

$$C_8H_{14}<\begin{matrix}CO_2Me\\CO_2H\end{matrix} \longrightarrow C_8H_{14}<\begin{matrix}CO_2Me\\COCl\end{matrix} \longrightarrow C_8H_{14}<\begin{matrix}CO\\CH_2\end{matrix}>O.$$

This substance should yield epicamphor by a process similar to that by which camphor had been obtained, but, unfortunately, all attempts to bring about combination between β-campholide and potassium cyanide were unsuccessful. An investigation which is of special importance in connexion with the present communication was published by Wagner in 1903 (*Chem. Zeit.*, **27**, 271; compare *Ber.*, 1903, **36**, 4602), since he there describes the preparation and derivatives of a substance which he claims to be epicamphor (β-camphor). Wagner subjected bornylene to the action of acetic acid and sulphuric acid, and thus converted it, by the well known Bertram and Walbaum process (*J. pr. Chem.*, 1894, [ii], **49**, 1), into a substance which he considered was the acetyl derivative of β-borneol:

$$\underset{\text{Bornylene.}}{C_8H_{14}<\begin{matrix}CH\\\|\\CH\end{matrix}} \longrightarrow \underset{\beta\text{-Bornyl acetate.}}{C_8H_{14}<\begin{matrix}CH\cdot O\cdot CO\cdot CH_3\\|\\CH_2\end{matrix}}$$

This substance distilled at 229—230°/755 mm., and gave, on hydrolysis, the corresponding borneol (m. p. 203—204°), and, by oxidising this with permanganate, a ketone was obtained which distilled at 207—208°, melted at 160—161°, and this Wagner assumed to be β-camphor. He also prepared the oxime (m. p. 119—119·5°) and the semicarbazone (m. p. 201—202°).

The investigation of *l*-epicamphor, described in the present communication, shows, however, that the properties of this substance are in reality quite different from those of the substance obtained by Wagner.

l-Epicamphor melts at 183·5—184°, distils at 212°, yields an oxime melting at 103—104° and a semicarbazone melting at 236—238°, and *l*-epiborneol melts at 182°.

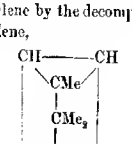
On the other hand, camphor melts at 179°, distils at 207°, yields an oxime melting at 119° and a semicarbazone melting at 246—248°, and borneol melts at 203°.

The researches of Bredt (*Annalen*, 1909, **366**, 52) have shown conclusively that the hydrocarbon employed by Wagner in his experiments could not have been pure bornylene, but must have been a mixture of bornylene and camphene or cyclene.*

There can therefore be little doubt that the ketone obtained by Wagner consisted largely of impure camphor, and this view is borne out by some of the physical properties which he ascribed to his product and its derivatives. In order to obtain further evidence on this point, Bredt and Hilbing (*J. pr. Chem.*, 1911, [ii], **84**, 783) investigated the addition of acetic acid to pure bornylene, and obtained a large yield (86 per cent.) of an ester distilling at 103—104°/14 mm., but this was not a single substance, since it yielded on hydrolysis a mixture of borneols melting at 175—178°, which could not be separated by fractional crystallisation, and the only substance that could be obtained by the oxidation of this mixture was camphor.

Before proceeding to a description of the methods by which *l*-epicamphor may now be obtained, some of the processes which were tried without success may be briefly mentioned. In the first place, *d*-bornylene-3-carboxylic acid was reduced to camphan-3-carboxylic acid (p. 2198); the amide of this was prepared, and submitted to the Hofmann reaction with the object of obtaining β-bornylamine, from which, by the action of nitrous acid, β-borneol

* Tschugaev (*Annalen*, 1912, **388**, 280) considers that the by-product obtained during the preparation of bornylene by the decomposition of methyl bornyl xanthate, $C_{10}H_{17}O \cdot CS_2Me$, consists of cyclene,



It is remarkable that this hydrocarbon, which is so stable to permanganate that it may be purified by oxidising the mixture with bornylene with permanganate until the latter hydrocarbon is destroyed (compare Henderson and Caw, T., 1912, **101**, 1416), should be oxidised by hydrogen peroxide more readily than bornylene.

(epiborneol) should result, and be converted, by oxidation, into epicamphor:

$$C_8H_{14}<\begin{array}{l}C\cdot CO_2H\\ \| \\ CH\end{array} \longrightarrow C_8H_{14}<\begin{array}{l}CH\cdot CO_2H\\ | \\ CH_2\end{array} \longrightarrow C_8H_{14}<\begin{array}{l}CH\cdot CO\cdot NH_2\\ | \\ CH_2\end{array} \longrightarrow$$

$$C_8H_{14}<\begin{array}{l}CH\cdot NH_2\\ | \\ CH_2\end{array} \longrightarrow C_8H_{14}<\begin{array}{l}CH\cdot OH\\ | \\ CH_2\end{array} \longrightarrow C_8H_{14}<\begin{array}{l}CO\\ | \\ CH_2\end{array}.$$

Experiment showed that a basic substance is actually obtained in this way, and this reacted with nitrous acid, but the product proved to be a mixture of borneols, and attempts to separate these have, so far, been unsuccessful. *d*-Bornylene-3-carboxylic acid itself was next converted into the amide in the hope that, by the careful application of the Hofmann reaction, this might yield the β-aminobornylene which Duden and Macintyre (*loc. cit.*) had endeavoured to prepare, since this substance would doubtless react with nitrous acid to yield epicamphor:

$$C_8H_{14}<\begin{array}{l}C\cdot CO\cdot NH_2\\ \| \\ CH\end{array} \longrightarrow C_8H_{14}<\begin{array}{l}C\cdot NH_2\\ \| \\ CH\end{array} \longrightarrow C_8H_{14}<\begin{array}{l}CO\\ | \\ CH_2\end{array}.$$

These various interactions resulted in the formation of a small quantity of a neutral substance, which was quite homogeneous, melted at 135°, and was evidently a ketone, since it reacted readily with phenylhydrazine. Examination showed, however, that it contained halogen, and it is probable that this substance was bromoepicamphor (p. 2210), which melts at the same temperature. Many other processes, which seemed likely to lead to the formation of epicamphor, were also investigated, but it is unnecessary to discuss these here. The first published account of the preparation of *l*-epicamphor is contained in a notice by F. R. Lankshear and W. H. Perkin, jun. (P., 1911, **27**, 167), in which it is shown that this substance may be obtained from *d*-camphane-3-carboxylic* acid by the following process. The chloride of this acid is treated with bromine, the product poured into alcohol, and the bromo-ester thus obtained digested with potassium acetate in acetic acid solution. After hydrolysis with alcoholic potassium hydroxide, the crude α-hydroxycamphane-3-carboxylic acid is oxidised by lead peroxide.

* In order that the letters α- and β- may be reserved in the usual manner for indicating the position of substituents in relation to the carboxyl group, the following scheme of nomenclature for the camphane- and bornylene-carboxylic acids has been adopted:

$C_8H_{14}<\begin{array}{l}CH\cdot CO_2H\\ CH_2\end{array}$	$C_8H_{14}<\begin{array}{l}CH_2\\ CH\cdot CO_2H\end{array}$	$C_8H_{14}<\begin{array}{l}C\cdot CO_2H\\ \| \\ CH\end{array}$	$C_8H_{14}<\begin{array}{l}CH\\ C\cdot CO_2H\end{array}$
Camphane-3-carboxylic acid.	Camphane-2-carboxylic acid.	Bornylene-3-carboxylic acid.	Bornylene-2-carboxylic acid.

permanganate, or chromic acid, when *l*-epicamphor is obtained according to the scheme:

$$C_8H_{14}<\begin{matrix}CH\cdot CO_2H\\ CH_2\end{matrix} \rightarrow C_8H_{14}<\begin{matrix}CBr\cdot CO_2H\\ | \\ CH_2\end{matrix} \rightarrow C_8H_{14}<\begin{matrix}C(OAc)\cdot CO_2H\\ | \\ CH_2\end{matrix}$$

$$C_8H_{14}<\begin{matrix}C(OH)\cdot CO_2H\\ | \\ CH_2\end{matrix} \rightarrow C_8H_{14}<\begin{matrix}CO\\ | \\ CH_2\end{matrix}.$$

The first specimens of *l*-epicamphor, obtained in this way, were too small to allow of purification by means of the semicarbazone or by recrystallisation, and the melting point given (about 165°) was that of the crude product. Subsequently, considerable quantities (30 grams) were prepared by this process, and the purified substance then melted at 178—182°, had α_D $-57\cdot9$, and yielded an oxime melting at 103° and a semicarbazone melting at 236°. While these researches were in progress, Bredt and his co-workers had also succeeded in preparing *l*-epicamphor by a different method, and a preliminary account of this investigation appeared in the same year (*Chem. Zeit.*, 1911, **35**, 765). The process which these investigators employed was the conversion of *d*-bornylene-3-carboxylic acid, through the acid chloride, into the hydrazide, which, when subjected to the Curtius method, yielded the azide, and from this, by boiling with hydrochloric acid, *l*-epicamphor was obtained:

$$C_8H_{14}<\begin{matrix}C\cdot COCl\\ \| \\ CH\end{matrix} \rightarrow C_8H_{14}<\begin{matrix}C\cdot CO\cdot NH\cdot NH_2\\ \| \\ CH\end{matrix} \rightarrow C_8H_{14}<\begin{matrix}C\cdot CO\cdot N_3\\ \| \\ CH\end{matrix}$$

$$C_8H_{14}<\begin{matrix}C\cdot NH_2\\ \| \\ CH\end{matrix} \text{ or } C_8H_{14}<\begin{matrix}C{:}NH\\ | \\ CH_2\end{matrix} \rightarrow C_8H_{14}<\begin{matrix}CO\\ | \\ CH_2\end{matrix}.$$

Since epicamphor had been obtained simultaneously in the laboratories at Aachen and Manchester, it was thought that the best plan would be to join forces; this was done, and the present publication is the result of that arrangement. Of the two processes just indicated for the preparation of *l*-epicamphor, the azide method is much to be preferred, because it not only gives much better yields, but also a purer product. It has this serious drawback, however, that there is always danger of explosion during the formation and extraction of the azide, and the process can therefore only be carried out safely with comparatively small quantities of material. For these reasons a large number of experiments were made with the object of devising a more satisfactory process for the preparation of epicamphor than either of those mentioned above, and, after many failures, this was ultimately accomplished with the aid of d-*bornylene*-3-*hydroxamic acid*.

This acid is produced almost quantitatively when methyl

d-bornylene-3-carboxylate is treated with hydroxylamine in the presence of sodium methoxide (compare Lossen, *Annalen*, 1875, **175**, 313; **178**, 213; Thiele and Pickard, *Annalen*, 1899, **309**, 189); it is a crystalline substance, and is remarkable for the ease with which it is converted into *l*-epicamphor under a variety of conditions. When a small quantity of the acid is heated alone, it decomposes just above its melting point (136°), with almost explosive violence and development of much heat; ammonia, and steam are liberated, and epicamphor is formed. The principal product of the decomposition is, however, a pale yellow, transparent resin, which may be distilled, and this, in contact with hydrochloric acid and subsequent distillation in steam, gives a large yield of epicamphor.

The explanation of this curious decomposition is probably the following: Bornylene-3-hydroxamic acid on heating loses water, the product undergoes molecular rearrangement, and the yellow, volatile resin is bornylene 3-*iso*cyanate. The water produced during this process decomposes some of the *iso*cyanate, with formation of epicamphor and ammonia, and the remainder is decomposed in the same direction by the subsequent treatment with hydrochloric acid and distillation in steam:

$$C_8H_{14}\Big<\begin{matrix}C\cdot C(OH){:}N\cdot OH\\ \| \\ CH\end{matrix} \longrightarrow C_8H_{14}\Big<\begin{matrix}C\cdot N{:}C{:}O\\ \| \\ CH\end{matrix} \longrightarrow$$

Bornylene-3-hydroxamic acid. Bornylene 3-*iso*cyanate.

$$C_8H_{14}\Big<\begin{matrix}C\cdot NH\cdot CO_2H\\ \| \\ CH\end{matrix} \qquad C_8H_{14}\Big<\begin{matrix}C\cdot NH_2\\ \| \\ CH\end{matrix} \longrightarrow$$

Bornylene-3-carbamic acid.

$$C_8H_{14}\Big<\begin{matrix}C{:}NH\\ | \\ CH_2\end{matrix} \longrightarrow C_8H_{14}\Big<\begin{matrix}CO\\ | \\ CH_2\end{matrix}.$$

The sodium salt of *d*-bornylenehydroxamic acid also decomposes with considerable violence at as low a temperature as 105°, and the product, on treatment with hydrochloric acid, yields *l*-epicamphor, and, again, the aqueous solution of the sodium salt gradually clouds when it is boiled, owing to the separation of epicamphor. These pyrogenetic decompositions, owing to their violence, are not suitable as methods of preparation of epicamphor, but the discovery that the acetyl and benzoyl derivatives of *d*-bornylenehydroxamic acid, which decompose in a similar manner, do so more quietly, led ultimately to the working out of a valuable method for the preparation of epicamphor, which consists in bringing about the intramolecular change mentioned above, with the aid of toluene-*p*-sulphonyl chloride and several hundred grams of *l*-epicamphor have been made in this way (compare p. 2206).

This method of preparation gives a good yield of *l*-epicamphor,

and its great advantage over the azide process (p. 2187) lies in the fact that it proceeds without the risk of explosion, and may therefore be carried out with comparatively large quantities of material.

All the methods for obtaining *l*-epicamphor which are at present available have *d*-bornylene-3-carboxylic acid for their starting point, and not only is the preparation of this acid a long and tedious process, but its subsequent conversion into epicamphor involves a complicated series of reactions, and thus, with ordinary laboratory apparatus, several months are required in order to prepare two or three hundred grams of epicamphor.

It is therefore to be hoped that the further experiments on which we are at present engaged will lead to the discovery of a simpler method for the preparation of this important substance.

Comparison of the Properties of l-*Epicamphor with those of* d-*Camphor.*

l-Epicamphor has an odour very similar to, but yet distinct from, that of camphor, it melts at 182°, distils at 213°, and is lævorotatory, the value for α_D in benzene being $-58{\cdot}21°$; epicamphoroxime melts at 103—104°, and has α_D $+100{\cdot}5°$; epicamphorsemicarbazone melts at 237—238°; on oxidation, epicamphor yields *d*-camphoric acid.

d-Camphor melts at 177—178°, distils at 207°, and has α_D $-39{\cdot}1°$ in benzene; the oxime melts at 119°, and has α_D $-56{\cdot}0°$, and the semicarbazone melts at 247—248°.* When *l*-epicamphor is treated, in ethereal solution, with *iso*amyl nitrite and sodamide, it yields the two stereoisomeric iso*nitroso*-l-*epicamphors*,

$$C_8H_{14}<\begin{matrix}CO\\ |\\ C{:}N{\cdot}OH\end{matrix},$$

the α-modification melts at 168—170° and has α_D $-201{\cdot}9°$, and the β-modification melts at 138—140°, and has α_D $-183{\cdot}5°$, and of these the latter is the unstable form, since it is converted into the former by melting or boiling with water. These two *iso*nitroso-*l*-epicamphors have also recently been prepared by Forster and Spinner by another process (T., 1912, **101**, 1348), and correspond with the two *iso*nitrosocamphors, $C_8H_{14}<\begin{matrix}C{:}N{\cdot}OH\\ |\\ CO\end{matrix}$, which melt at 152—153° and 114°, and have respectively α_D $+196{\cdot}6°$ and

* The semicarbazone of camphor was first prepared by Tiemann (*Ber.*, 1895, **28**, [illegible]), who stated that it melts at 236—238°, and this is usually given as the actual melting point. Rimini (*Gazzetta*, 1900, **30**, 603) pointed out, however, that the true melting or decomposing point is 245°, and we have prepared this substance in different ways and also find that it melts and decomposes at 245° or 247—248° (corr.)

$+172{\cdot}9^\circ$, and in this case also the higher melting isomeride is the stable form, since it is readily formed from the isomeride of lower melting point by the action of heat. The α- and β-modifications of *iso*nitroso-*l*-epicamphor both yield camphorquinone on treatment with formaldehyde and hydrochloric acid, and are converted into the imide of *d*-camphoric acid by heating with sulphuric acid, and these are reactions which are also shown by the *iso*nitroso-camphors.

Reduction with zinc dust and sodium hydroxide converts both α- and β-*iso*nitroso-*l*-epicamphor into the same *amino*-l-*epicamphor*, $C_8H_{14}<\genfrac{}{}{0pt}{}{CO}{CH{\cdot}NH_2}$, which melts at 168—170°, has, in benzene, α_D $+15^\circ$, and is a substance which crystallises well, and is comparatively stable, whereas aminocamphor, $C_8H_{14}<\genfrac{}{}{0pt}{}{CH{\cdot}NH_2}{CO}$, melts at 226—228°, and is a waxy substance, which readily undergoes change (compare Duden and Pritzkow, *Annalen*, 1899, **307**, 209).

l-Epicamphor is readily reduced when sodium is dissolved in its boiling alcoholic solution, with the formation of l-*epiborneol*, $C_8H_{14}<\genfrac{}{}{0pt}{}{CH{\cdot}OH}{CH_2}$, a crystalline substance, which melts at 181—182·5°, and yields a phenylurethane melting at 82°. It is remarkable that epiborneol has no rotation, but it is not really an inactive substance, as is shown by the fact that, when it is converted by loss of water into the hydrocarbon, the substance which results is *l*-bornylene, with the rotation α_D $-18{\cdot}45^\circ$.

For the purpose of the elimination of water, *l*-epiborneol was converted, by the action of sodium and then of carbon disulphide, into *l*-epibornyl xanthate, and then, by treatment with methyl iodide, into methyl *l*-epibornyl xanthate, which, on distillation, is decomposed with elimination of methyl mercaptan and carbonyl sulphide, and formation of *l*-bornylene (method of Tschugaev):

$$C_8H_{14}<\genfrac{}{}{0pt}{}{CH{\cdot}OH}{CH_2} \longrightarrow C_8H_{14}<\genfrac{}{}{0pt}{}{CH{\cdot}O{\cdot}CS_2Na}{CH_2} \longrightarrow$$

$$C_8H_{14}<\genfrac{}{}{0pt}{}{CH{\cdot}O{\cdot}CS_2Me}{CH_2} = C_8H_{14}<\genfrac{}{}{0pt}{}{CH}{CH} + MeSH + COS.$$

The *l*-bornylene, produced in this way, melted at 114°, and had, in solution in toluene, α_D $-18{\cdot}45^\circ$; it yielded *d*-camphoric acid on oxidation, and was evidently identical with the *l*-bornylene which Bredt (*Annalen*, 1909, **366**, 46) had previously obtained by the decomposition of sodium β-bromodihydrobornylenecarboxylate by boiling with water:

$$C_8H_{14}<\begin{matrix}CH\cdot CO_2Na\\ |\\ CHBr\end{matrix} = C_8H_{14}<\begin{matrix}CH\\ \|\\ CH\end{matrix} + C_8H_{14}<\begin{matrix}C\cdot CO_2H\\ \|\\ CH\end{matrix} + CO_2 + 2NaBr.$$

During the experiments on the reduction of *l*-epicamphor with sodium and alcohol we have endeavoured to determine whether, besides *l*-epiborneol, a second isomeride (*epi*iso*borneol*) is produced, and, although the melting points of different specimens varied slightly and seemed to indicate that such a substance might be present, if this is the case, it must be present in small quantity, and we have not been able to isolate it. Bertram and Wahlbaum (*J. pr. Chem.*, 1894, [ii], **49**, 12; compare Wallach, *Annalen*, 1885, **230**, 225) have shown that the product of the reduction of camphor with sodium and alcohol contains, besides *d*-borneol, sometimes as much as 20 per cent. of *l*-*iso*borneol.

d-Borneol melts at 208°, has α_D + 38·39°, and, like *l*-epiborneol, yields *l*-bornylene when it is converted into the methyl xanthate, and this is distilled. *l*-*iso*Borneol, obtained from *d*-camphor by reduction, melts at 212°, and has α_D −33°.

If the formulæ of camphor and epicamphor are compared it is

$$\begin{matrix}CH_2\cdot CH\text{---}CH_2\\ \quad CMe_2\\ CH_2\cdot CMe\text{---}CO\\ \text{Camphor.}\end{matrix} \quad \text{and} \quad \begin{matrix}CH_2\cdot CH\text{---}CO\\ \quad CMe_2\\ CH_2\cdot CMe\text{---}CH_2\\ \text{Epicamphor.}\end{matrix},$$

at once evident that, apart from the relative positions of the carbonyl and methylene groups, the most striking difference is that one of the linkings of the carbonyl group is attached to the tertiary CMe group in the case of camphor, whereas, in epicamphor, it is attached to the secondary >CH group, and it was therefore to be expected that the carbonyl group of epicamphor might show greater reactivity than that in camphor. It is well known that camphor does not combine with hydrogen cyanide, but we were surprised to find that, in spite of the presence of the $>CH\cdot CO\cdot CH_2$- group in epicamphor, this substance is also not capable of yielding an additive product with hydrogen cyanide, at all events, under the favourable conditions described on p. 2210. This is the more remarkable since Lapworth and Chapman (T., 1901, **79**, 378) have shown that the >CO group in camphorquinone combines quite readily with hydrogen cyanide; again, Manasse (*Ber.*, 1897, **30**, 662) has shown that camphorquinone may be reduced by zinc dust and acetic acid, whereas epicamphor is unchanged under the same conditions, and these results seem to indicate that any difference

in the relative reactivity of the carbonyl groups in camphor and epicamphor is, at the most, only a slight one.

Another consideration connected with the difference in the constitutional formulæ of camphor and epicamphor is the possibility that the presence of the $>CH$ group adjacent to the carbonyl group in epicamphor and its absence in camphor might well lead to a difference in the constitution of the substitution derivatives, and that, for example, whilst bromocamphor and camphorcarboxylic acid contain the groupings $-CHBr\cdot CO-$ and $-CH(CO_2H)\cdot CO-$, the corresponding derivatives of epicamphor might have the following constitutions:

$$\begin{array}{l} CH_2\cdot CBr\text{---}CO \\ \qquad | \\ \qquad CMe_2 \\ \qquad | \\ CH_2\cdot CMe\text{---}CH_2 \end{array} \quad \text{and} \quad \begin{array}{l} CH_2\cdot C(CO_2H)\cdot CO \\ \qquad | \\ \qquad CMe_2 \\ \qquad | \\ CH_2\cdot CMe\text{----}CH_2 \end{array} .$$

The sodium salt of *l*-epicamphorcarboxylic acid is produced when a boiling ethereal solution of *l*-epicamphor is treated with carbon dioxide in the presence of sodium, but it is more readily obtained and in much better yield when the solution of epicamphor in benzene is boiled with sodamide and a stream of carbon dioxide passed (p. 2214). The free acid melts at 120—122°, and is very similar in properties to *d*-camphorcarboxylic acid (m. p. 125—126°), since both acids are decomposed somewhat above their melting points into carbon dioxide and epicamphor or camphor respectively. Epicamphorcarboxylic acid gives a green coloration when ferric chloride is added to its alcoholic solution (camphorcarboxylic acid gives a blue in similar circumstances), and it therefore is clear that it must contain the grouping $>CH\cdot CO_2H$, and its formula must be $C_8H_{14}<\begin{matrix}CO\\ |\\ CH\cdot CO_2H\end{matrix}$, and not that suggested above as a possible alternative. When this acid is treated with bromine at the ordinary temperature it yields bromo-*l*-epicamphorcarboxylic acid (m. p. 145°) and, as this acid gives no coloration with ferric chloride, its constitution must be that represented by the formula $C_8H_{14}<\begin{matrix}CO\\ |\\ CBr\cdot CO_2H\end{matrix}$.

Now this acid is decomposed when it is heated a few degrees above its melting point with elimination of carbon dioxide and formation of a bromo-*l*-epicamphor, which melts at 130°, has α_D $-86.6°$ (bromocamphor melts at 76° and has α_D $+140°$), and the constitution of this substance must evidently be $C_8H_{14}<\begin{matrix}CO\\ |\\ CH\cdot Br\end{matrix}$, a view which is confirmed by the fact that it yields *d*-camphoric acid when it is oxidised by dilute nitric acid. This same bromo-

picamphor, however, is also obtained by the direct bromination f epicamphor (p. 2210), and it follows, therefore, that hydrogen f the $>CH_2$ group, and not of the $\geq CH$ group, is substituted uring the conversion of epicamphor into epicamphorcarboxylic cid and bromoepicamphor.

The l-*Epiborneolcarboxylic Acids,* l-*Bornylene-2-carboxylic Acid,* l-*Camphane-2-carboxylic Acid, and the Conversion of* l-*Epi-camphor into* d-*Camphor.*

Roser, in 1885 (*Ber.*, **18**, 3114), first called attention to the act that camphorcarboxylic acid, although it is a β-ketonic acid, annot be reduced by sodium amalgam, and showed that reduction oes not even take place under the conditions which so readily onvert camphor into borneol, namely, when the acid or its ester s treated with sodium and alcohol. These observations were con-rmed by Bredt (*Annalen*, 1906, **348**, 200; 1909, **366**, 1), who iscovered, however, that camphorcarboxylic acid may be reduced lectrolytically, using potassium amalgam as the cathode, and that t then yields two acids, namely, *cis*-borneolcarboxylic acid (m. p. 01—102°) and *cis-trans*-borneolcarboxylic acid (m. p. 171°), whereas four isomeric acids of the formula $C_8H_{14}<\begin{matrix}CH\cdot CO_2H\\ CH\cdot OH\end{matrix}$ are theoretically possible.

Owing to the difference in constitution between epicamphorcarb-oxylic acid and camphorcarboxylic acid (compare p. 2192), it eemed possible that the former might exhibit less resistance to educing agents than the latter, and experiment showed that picamphorcarboxylic acid is actually reduced when the solution f its sodium salt is boiled with sodium amalgam, but the process s very slow and incomplete.

When, however, *l*-epicamphorcarboxylic acid was reduced electro-lytically under the same conditions as camphorcarboxylic acid, it was more readily reduced than the latter, and yielded a product from which, by fractional crystallisation from light petroleum, four *l*-epiborneolcarboxylic acids, $C_8H_{14}<\begin{matrix}CH\cdot OH\\ CH\cdot CO_2H\end{matrix}$, were separ-ated, namely, A (m. p. 125°, α_D $+2\cdot36°$), B (m. p. 143—145°, α_D $-4\cdot8°$), C (m. p. 173°, α_D $+15\cdot18°$), and D (m. p. 237°, α_D $-77\cdot9°$).* When a mixture of these acids is dehydrated with

* The results of analysis indicate that this isomeride of high melting point (D) may possibly be a pinacone acid of the formula

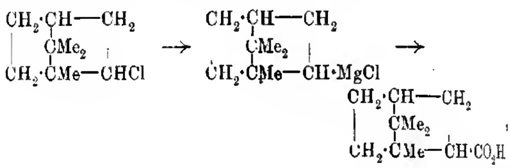
$$C_8H_{14}<\begin{matrix}C(OH)\text{——}(OH)C\\ CH\cdot CO_2H \quad CO_2H\cdot CH\end{matrix}>C_8H_{14},$$

but this seems improbable in view of the fact that it dissolves almost as readily in

acetyl chloride and the product distilled, l-*bornylene-2-carboxylic acid*, $C_8H_{14}<\begin{matrix}CH\\ \Vert\\ C\cdot CO_2H\end{matrix}$, is obtained, which melts at 115°, has α_D −95·7°, and is very similar to *d*-bornylene-3-carboxylic acid, $C_8H_{14}<\begin{matrix}C\cdot CO_2H\\ \Vert\\ CH\end{matrix}$, (m. p. 112°, α_D +149·5°), in its properties.

l-*Camphane-2-carboxylic acid*, $C_8H_{14}<\begin{matrix}CH_2\\ \vert\\ CH\cdot CO_2H\end{matrix}$, is obtained in quantitative yield when *l*-bornylene-2-carboxylic acid is reduced by hydrogen in the presence of palladium and gum arabic (compare p. 2219); it melts at 78—80°, has α_D −37·8°, and closely resembles *d*-camphane-3-carboxylic acid, $C_8H_{14}<\begin{matrix}CH\cdot CO_2H\\ \vert\\ CH_2\end{matrix}$, which melts at 90—91°, and is produced by the reduction of *d*-bornylene-3-carboxylic acid under the same conditions (p. 2198).

Epicamphane-2-carboxylic acid had already been prepared by Houben and Kesselkaul (*Ber.*, 1902, **35**, 3696) from pinene hydrochloride by conversion into the magnesium derivative and subsequent decomposition by carbon dioxide and water:



and these investigators state that the free acid crystallises and distils at 156°/12 mm. Zelinsky (*Ber.*, 1902, **35**, 4417; compare *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 646) prepared the same acid (called by him "camphanecarboxylic acid") from borneol by converting it into bornyl iodide, and then acting on this with magnesium and carbon dioxide, and he states that it melts at 69—71°. At a later date, Houben (*Ber.*, 1905, **38**, 3799) again prepared the acid (hydropinenecarboxylic acid) from pinene hydrochloride, and describes it as a crystalline substance, melting at 72—74° and distilling at 153°/13 mm.

Methyl *l*-bornylene-2-carboxylate reacts readily with hydroxylamine in the presence of sodium methoxide, with the formation of l-*bornylene-2-hydroxamic acid*, a syrup which, on heating, decomposes vigorously, and yields steam, ammonia, some camphor, and a pale yellow, resinous substance. The latter, which doubtless consists of bornylene 2-*iso*cyanate, gives a large yield of *d*-camphor

solvents as the other isomerides, and that an acid of this kind has not been observed among the products of the reduction of camphorcarboxylic acid.

when it is mixed with hydrochloric acid and distilled in steam, and the whole process, which may be represented thus:

$$C_8H_{14}<\begin{matrix}CH\\ \|\\ C\cdot C(OH){:}N\cdot OH\end{matrix} \longrightarrow C_8H_{14}<\begin{matrix}CH\\ \|\\ C\cdot N{:}CO\end{matrix}$$

Bornylene-2-hydroxamic acid. Bornylene 2-*iso*cyanate.

$$C_8H_{14}<\begin{matrix}CH\\ \|\\ C\cdot NH_2\end{matrix} \longrightarrow C_8H_{14}<\begin{matrix}CH_2\\ |\\ C{:}NH\end{matrix} \longrightarrow C_8H_{14}<\begin{matrix}CH_2\\ |\\ CO\end{matrix}$$

Camphor.

is exactly similar to the formation of *l*-epicamphor from *l*-bornylene-3-hydroxamic acid under the same conditions. Lastly, the above intramolecular change was brought about by treating the sodium salt of *l*-bornylene-2-hydroxamic acid with toluene-*p*-sulphonyl chloride (compare p. 2221), and, after decomposing with hydrochloric acid, the product was distilled in steam, when a comparatively large yield of *d*-camphor was obtained. The camphor resulting from these two experiments melted at 176°, and, in ethyl acetate solution, α_D +47·7°, and yielded an oxime melting at 119°, whereas ordinary *d*-camphor melts at 178°, has α_D +48·0°, and camphoroxime melts at 119°.

The conversion of *l*-bornylene-2-carboxylic acid into *d*-camphor completes the interesting cycle, *d*-camphor $\rightleftarrows$ *l*-epicamphor, and the whole scheme may be clearly represented thus:

d-Camphor

Camphorcarboxylic acid	*l*-Bornylene-2-hydroxamic acid
Borneolcarboxylic acid	*l*-Bornylene-2-carboxylic acid
Bornylene-3-carboxylic acid	*l*-Epiborneolcarboxylic acid
Bornylene-3-hydroxamic acid	*l*-Epicamphorcarboxylic acid

l-Epicamphor

Comparison of some Physiological Properties of d-*Camphor and* l-*Epicamphor.*

The following experiments, which deal with the comparative action of camphor and epicamphor on the beat of the heart in a frog, following the administration of chloral, were carried out by Professor van der Velden and Dr. P. Leyden in the laboratories of the Mediz. Klinik der Akademie für prakt. Mediz. in Düsseldorf.

The administration of a drop of a 5 per cent. oil solution of

camphor doubled the beat of the heart from thirteen to twenty-six, and the heart curve tracing was unusually regular; the same experiment with epicamphor showed no appreciable action. When a 10 per cent. oil solution of camphor was employed, it was found that three drops increased the beat from seven to twenty-two, and that the beat then became very constant, and the curve tracing was again remarkably regular. The same quantity of epicamphor increased the beat slowly from six to twelve, and then a gradual decrease was observed and the beat became very irregular.

The administration of three drops of a 20 per cent. oil solution of camphor increased the beat from six to eighteen; then a decrease to eleven occurred, and the well-known poisonous action of camphor became evident.

In a similar experiment with epicamphor the beat was increased from six to twenty-seven, but rapidly decreased to thirteen in five minutes. A subsequent administration had no further effect, and the curve, which at first was very regular, became weaker.

These results show that favourable action of epicamphor on the beat of the heart does not become apparent until the solution administered is about four times stronger than that which produces the same effect in the case of camphor. A further series of experiments has, moreover, clearly shown that, even at this concentration, epicamphor has not the same favourable action as camphor because the effect soon disappears, whereas in the case of camphor (provided that it is absolutely pure) the action induced persists for a much longer time. The action of camphor is toxic at the concentration necessary for favourable action in the case of epicamphor.

We are at present engaged in a further investigation of the properties and derivatives of epicamphor, and hope shortly to publish an account of the results of these experiments.

EXPERIMENTAL.*

d-*Bornylene-3-carboxylic Acid and its Derivatives.*

The preparation of bornylene-3-carboxylic acid from camphor-carboxylic acid by electrolytic reduction to the isomeric borneol-

* Wilhelm Hilhing and Joseph Regout assisted Prof. Bredt in Aachen, the former in the preparation of epicamphor by the bornylenecarboxylic acid azide method and in converting it into the oxime, semicarbazone, and into epicamphorcarboxylic acid by the sodium, carbon dioxide, process, and also in preparing several derivatives of bornylenecarboxylic acid, such as the ester, acid chloride and amide; the latter prepared most of the epiborneol employed in this research, and converted it into bornylene by the Tschugaev xanthate method.

Mr. F. R. Lankshear assisted Prof. Perkin by preparing much of the bornylene-

carboxylic acids and subsequent elimination of water, has already been described by Bredt and his co-workers (*Annalen*, 1906, **348**, 2; 1909, 366, 1).

The acid employed in the present research was purified by distillation either alone or in a current of steam or by recrystallisation from acetone, from which it separates in large, colourless crystals; it melts at 112—113°, distils at 156—157°/13 mm., and yields an anhydride, which melts at 96—97° and distils at 236°/21 mm.

The *barium* salt, $(C_{10}H_{15}\cdot CO_2)_2Ba,4H_2O$, was prepared by dissolving the acid in pure barium hydroxide, and, after removing the excess of the latter by carbon dioxide and concentrating the filtrate, the salt separated in needles. For analysis it was recrystallised from water, and then exposed to the air for several days:

0·2738, on drying at 120°, lost 0·0360 H_2O and gave 0·1112 $BaSO_4$. $H_2O=13·2$; $Ba=24·2$.

$(C_{11}H_{15}O_2)_2Ba,4H_2O$ requires $H_2O=12·7$ and $Ba=24·2$ per cent.

The *acid chloride*, $C_{10}H_{15}\cdot COCl$, may be prepared by adding the acid (20 grams) to phosphorus pentachloride covered with light petroleum (100 c.c., b. p. 35—60°), and after the vigorous decomposition has subsided, the whole heated on the steam-bath for two hours, the light petroleum distilled off, and the residue fractionated under diminished pressure.

This chloride may be prepared even more conveniently by warming equal weights of the acid and thionyl chloride; as soon as the reaction is complete, the product is distilled, when an almost quantitative yield of the pure chloride is obtained.

Bornylene-3-carboxyl chloride distils at 120—121°/19 mm., and is a comparatively stable substance, which fumes only slightly in the air:

0·2000 gave 0·1811 AgCl. Cl=17·3.

$C_{11}H_{15}OCl$ requires Cl=17·8 per cent.

The *acid amide*, $C_{10}H_{15}\cdot CO\cdot NH_2$.—This substance may be prepared from the anhydride by heating with concentrated aqueous ammonia at 100°, when a clear solution is obtained, from which the amide crystallises on cooling. A specimen was also prepared by gradually adding the acid chloride to concentrated aqueous ammonia, the whole being well cooled and stirred during the

[illegible] carboxylic acid used in Manchester for the preparation of epicamphor and by photographing the absorption spectra of epicamphor and its derivatives. Valuable assistance was also rendered by Messrs. Reginald Furness and Harold Goodwin, not only in the preparation of bornylenecarboxylic acid, but also in working out the [illegible] of the formation of epicamphor by the bornylenehydroxamic acid process, of the preparation of epicamphorcarboxylic acid by the sodamide—carbon dioxide method, and of the conversion of epicamphor into camphor.

operation. The amide is best crystallised from dilute ammonia, from which it at first frequently separates as a milky precipitate, but on rubbing or the addition of a crystal, crystallisation at once sets in. It melts at 119—122°, and yields a crystalline hydrochloride when its solution in light petroleum is saturated with hydrogen chloride, but this is unstable, and decomposes on keeping:

0·2367 gave 16 c.c. N_2 at 18° and 752 mm. N = 8·0.

$C_{11}H_{17}ON$ requires N = 7·8 per cent.

The *methyl* ester, $C_{10}H_{15}\cdot CO_2Me$.—The esters of bornylene-3-carboxylic acid must not be prepared by the action of the acid chloride on the alcohols or by saturating the alcoholic solutions of the acid with hydrogen chloride, because the esters obtained in both cases, although they distil constantly, invariably contain chlorine. The large quantities of the methyl ester used in this research were prepared as follows: The pure acid (10 grams), dissolved in methyl alcohol (50 grams) and sulphuric acid (5 grams), was left for twenty-four hours, and then heated on the steam-bath for two hours. After diluting with water, the ester was extracted with ether, washed with water and dilute sodium carbonate, dried, and distilled.

Under these conditions, esterification is practically complete, and the methyl ester distils at 158°/100 mm.:

0·1112 gave 0·3021 CO_2 and 0·0941 H_2O. C = 73·9; H = 9·4.

$C_{12}H_{18}O_2$ requires C = 74·2; H = 9·4 per cent.

1·6464, made up to 20 c.c. in ethyl acetate, gave α_D +100·5°.

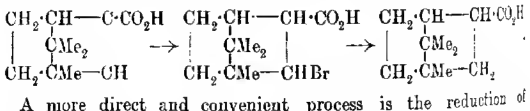
The *ethyl* ester, prepared in a similar manner, distils at 115°/12 mm. or 168°/100 mm.:

0·1211 gave 0·3330 CO_2 and 0·1079 H_2O. C = 74·9; H = 9·9.

$C_{13}H_{20}O_2$ requires C = 75·0; H = 9·6 per cent.

d-*Camphane-3-carboxylic Acid.*

Camphane-3-carboxylic acid was first prepared by Bredt (*Annalen*, 1909, **366**, 60) from *d*-bornylene-3-carboxylic acid by conversion into β-bromohydrobornylene-3-carboxylic acid (β-bromocamphane-3-carboxylic acid) and subsequent reduction by potassium amalgam:



A more direct and convenient process is the reduction of bornylenecarboxylic acid by hydrogen in the presence of palladium and gum arabic under the conditions recommended by Skita (*Ber.*, 1909, **42**, 1630).

Pure bornylene-3-carboxylic acid (10 grams) dissolved in methyl alcohol was mixed with 5 c.c. of a 20 per cent. gum arabic solution and 0·5 gram of palladium chloride; 150 c.c. of hot water was then added, and the whole placed in a long, narrow cylinder, and hydrogen passed for several hours. The product was rendered alkaline by sodium carbonate, the methyl alcohol and most of the water distilled off, the solution filtered, acidified, and the crude camphanecarboxylic acid, which separated as a crystalline mass, collected and distilled in steam. The acid, which was not quite stable to permanganate, was dissolved in sodium carbonate, mixed with powdered ice, and left in contact with excess of permanganate for half an hour; the permanganate was then destroyed by sulphur dioxide, and the filtrate from the manganese precipitate concentrated and acidified. Finally, the camphane-3-carboxylic acid was recrystallised from dilute acetic acid, from which it separated as a voluminous mass of thin plates, and melted at 90—92°:

0·1072 gave 0·2847 CO_2 and 0·0951 H_2O. C=72·4; H=9·9.

$C_{11}H_{18}O_2$ requires C=72·5; H=9·9 per cent.

Conversion of d-Camphane-3-carboxylic Acid into l-Epicamphor.

This process, which is discussed on p. 2186, may be carried out under the following conditions: *d*-Camphane-3-carboxylic acid (18 grams) is mixed with phosphorus pentachloride (22 grams) in a flask fitted with a ground-in air-tube, heated on the steam-bath until decomposition is complete, and, after cooling, bromine (18 grams) is added, and the whole transferred to a pressure-tube and gradually heated in a water-bath for several hours. The product, which is almost free from bromine, is poured into alcohol, and, after remaining for twenty-four hours, water is added and the bromo-ester extracted with ether.

The ethereal solution is thoroughly washed with water, carefully dried, evaporated, and the residue mixed in a reflux apparatus with glacial acetic acid (50 c.c.) and anhydrous potassium acetate (20 grams) and heated in the oil-bath to boiling for forty-five minutes, when potassium bromide separates in quantity and there is some darkening.

The product is diluted with water, extracted with ether, the ethereal solution washed well, evaporated, and left during twenty-four hours with a solution of potassium hydroxide (25 grams) in methyl alcohol.

After heating for three hours on the steam-bath, the methyl alcohol is removed by evaporation, the residue then acidified and extracted with ether, when, on evaporation, crude α-hydroxy-

camphane-3-carboxylic acid remains as a pale brown syrup, and *l*-epicamphor was obtained from this in three different ways:

I. *By Oxidation with Permanganate.*—The syrupy acid (5 grams) was dissolved in a slight excess of dilute potassium hydroxide, gradually mixed with permanganate (1·5 grams), and the whole heated on the steam-bath until oxidation was complete. After acidifying with sulphuric acid, the same quantity of permanganate was again added, and the whole distilled in a current of steam, when a semi-solid mass passed over, which consisted of a mixture of epicamphor and bornylene-3-carboxylic acid. The distillate was made alkaline with dilute potassium hydroxide, extracted with ether, the ethereal solution dried, and the ether removed by careful distillation with a column, when a buttery mass resulted (0·7 gram), which in contact with porous porcelain became quite dry and melted at 165° (compare Laukshear and Perkin, P., 1911, **27**, 166), and, on treatment with hydroxylamine hydrochloride and sodium acetate, yielded *l*-epicamphoroxime melting at 103° (p. 2208).

Subsequently, a larger quantity of *l*-epicamphor (30 grams) was prepared by this process, and purified by conversion into the semicarbazone (p. 2209); it then melted at 178—182°, and yielded the following results on analysis:

0·1071 gave 0·3089 CO_2 and 0·1034 H_2O. C=78·7; H=10·7.

$C_{10}H_{16}O$ requires C=79·0; H=10·5 per cent.

II. *By Oxidation with Chromic Acid.*—In this experiment crude hydroxycamphanecarboxylic acid (3 grams), dissolved in a little water, was gradually mixed with an aqueous solution of chromic acid (1 gram), care being taken that the temperature did not rise above 35°.

When the product was heated in a steam distillation apparatus, carbon dioxide was eliminated, and an oil passed over which had the pungent odour of epicamphor, and on cooling became a butter-like mass.

This was collected and left in contact with porous porcelain until dry; it then melted at about 165—167°, and was proved to consist of epicamphor by conversion into the oxime (m. p. 102°) and the semicarbazone (m. p. 235—237°).

III. *By Oxidation with Lead Peroxide.*—In this experiment the crude hydroxycamphanecarboxylic acid (7 grams) was mixed with water (5 c.c.) and acetic acid (100 c.c.); precipitated lead peroxide (20 grams) was then added, and, after boiling for ten minutes in a reflux apparatus, during which carbon dioxide was evolved, the whole was distilled in steam, when epicamphor distilled as a buttery mass, and a further small quantity was obtained by adding more

lead peroxide and continuing the distillation. The distillate was extracted with ether, the ethereal solution shaken with sodium carbonate, which removed a considerable quantity of bornylene-3-carboxylic acid, dried, and evaporated, when crude epicamphor (2 grams) was obtained, which, in contact with porous porcelain, became quite hard, and was identified as before by conversion into the oxime (m. p. 103°) and semicarbazone (m. p. 235—237°).

Preparation of l-*Epicamphor from* d-*Bornylene-3-carboxylic Acid by the Azide Method of Curtius.*

It is remarkable that the bornylene-3-carboxylic hydrazide, $C_{10}H_{15}\cdot CO\cdot NH\cdot NH_2$, necessary for this process is a substance which is very difficult to obtain except under certain very definite conditions.

In the first experiments, bornylenecarboxylic ester was treated with hydrazine hydrate in the usual manner (Curtius, *J. pr. Chem.*, 1894, [ii], 50, 275) in or without the presence of alcohol, in the cold and at the boiling temperature, but in no case was the normal hydrazide obtained, and the only crystalline product which could be isolated was always the dibornylene-3-carboxylic hydrazide, $C_{10}H_{15}\cdot CO\cdot NH\cdot NH\cdot CO\cdot C_{10}H_{15}$, a description of which is given below. The action of the acid chloride on hydrazine hydrate was next investigated in the hope that the equation:

$$C_{10}H_{15}\cdot COCl + 2N_2H_4,H_2O = C_{10}H_{15}\cdot CO\cdot NH\cdot NH_2 + N_2H_4,HCl + H_2O$$

might be realised, but, except when the unusual conditions described below were employed, the result was always a negative one.

Thus, for example, when bornylenecarboxyl chloride was rubbed in a mortar with excess of hydrazine hydrate, a rather vigorous reaction set in with considerable development of heat, and this was checked by keeping the containing vessel in a freezing mixture. After an hour the product was mixed with water, the solid collected, washed with water and dilute sodium carbonate, and then crystallised from benzene or dilute alcohol, from which it separated as a glistening mass of needles, which became soft at 218° and melted at about 221°:

0·1326 gave 0·3623 CO_2 and 0·1083 H_2O. C = 74·5; H = 9·0.
0·1428 „ 10·4 c.c. N_2 at 17° and 745 mm. N = 8·2.
$C_{22}H_{32}O_2N_2$ requires C = 74·2; H = 9·0; N = 7·8 per cent.

Di-d-bornylene-3-carboxylic hydrazide,

$$C_{10}H_{15}\cdot CO\cdot NH\cdot NH\cdot CO\cdot C_{10}H_{15},$$

is almost insoluble in water, but readily so in alcohol, and is a remarkably stable substance, since it is only very slowly decomposed when digested with alcoholic potassium hydroxide or hydrochloric acid.

Ultimately, normal *d*-bornylene-3-carboxylic hydrazide,

$$C_{10}H_{15}\cdot CO\cdot NH\cdot NH_2,$$

was obtained, in almost quantitative yield, by adding an alcoholic solution of hydrazine hydrate to an ethereal solution of the acid chloride under the following conditions: The pure acid chloride (20 grams), dissolved in dry ether (150 grams) and cooled to 0°, is gradually added from a jacketed funnel containing a freezing mixture to a solution of hydrazine hydrate (15 grams) in alcohol, which must be cooled below 0°. The liquid soon becomes milky, and needle-shaped crystals of hydrazine hydrochloride form on the sides of the vessel. After several hours, the clear solution is decanted from this salt and evaporated under diminished pressure, when a syrupy residue is obtained, which readily crystallises, and this mass is left for some days over concentrated sulphuric acid to remove the remainder of the alcohol. The white mass (19·5 grams) is almost pure, and may be recrystallised from benzene or a mixture of benzene and light petroleum, from which it separates in needles:

0·1944 gave 25·9 c.c. N_2 at 16·5° and 738 mm. N=14·9.

$C_{11}H_{18}ON_2$ requires N=14·4 per cent.

d-*Bornylene-3-carboxylic hydrazide* melts at 109—110°, and is readily soluble in alcohol, but sparingly so in ether or cold water; it dissolves readily in dilute hydrochloric acid, and is reprecipitated on the addition of sodium carbonate. The *hydrochloride*, which was required for the preparation of the azide, was obtained by dissolving the hydrazide (20 grams) in alcohol (25 grams) and adding a solution of alcoholic hydrogen chloride saturated at 0° (60 grams), when the hydrochloride separated at once. After remaining for two hours in ice-water, the crystalline precipitate was collected, washed with a little alcoholic hydrogen chloride, and left over solid potassium hydroxide in a vacuum desiccator for two days:

0·2210 gave 0·1380 AgCl. Cl=15·4.

$C_{11}H_{18}ON_2,HCl$ requires Cl=15·38 per cent.

This hydrochloride melts and decomposes at 202°, and may be recrystallised either from water or alcohol, or best from a mixture of both. In a series of experiments the yields of the hydrazide and its hydrochloride from bornylenecarboxylic acid were the following:

One hundred grams of bornylenecarboxylic acid gave 103 grams of acid chloride (94 per cent.); this yielded 95 grams of hydrazide (94 per cent.), and from this, 103 grams of hydrochloride (92 per cent.) were obtained, or, the yield of hydrazide hydrochloride from 100 grams of bornylenecarboxylic acid is 80·6 per cent. of that theoretically possible.

Conversion of d-*Bornylene-3-carboxylic Hydrazide into* l-*Epicamphor.*

This experiment, which, owing to the well-known explosive nature of the azides, must be very carefully made and with small quantities of material, has been repeatedly carried out without accident under the following conditions: The hydrochloride of the hydrazide (14 grams) dissolved in water (200 c.c.) is covered with a layer of ether (100 c.c.), and the whole cooled in ice and salt. Sodium nitrite (3·1 grams) dissolved in a little water is then gradually added drop by drop, the temperature being maintained at 0° during the whole operation.

The addition of the nitrite produces a milkiness in the aqueous solution, but, by shaking, the oily azide passes into the ether, and at the end of the operation a few drops of dilute hydrochloric acid are added in order to ensure that nitrous acid is present in slight excess. The ethereal solution is separated, the aqueous layer extracted once with ether, and the combined extracts washed with ice-water, dried rapidly over calcium chloride, and mixed with alcohol (100 c.c.).

The ether is now removed on the steam-bath, and the alcoholic solution boiled in a reflux apparatus for two hours, and, after the alcohol has been distilled off under diminished pressure, a yellow syrup remains, which doubtless consists of the corresponding urethane.

This is dissolved in concentrated hydrochloric acid, and, after a few minutes, the solution is mixed with ice-water, when epicamphor separates in white flocks, and is best purified by distillation in steam, during which operation the bulk of the epicamphor, together with some bornylenecarboxylic acid, crystallises in the condenser. The whole is dissolved in ether, the bornylenecarboxylic acid carefully removed by repeated shaking with sodium carbonate, the ethereal solution dried, the ether slowly distilled off,* and the crude epicamphor left exposed to air with constant stirring until the residual ether has evaporated, and then placed in contact with porous porcelain, or the epicamphor may be directly distilled.

The yield of this nearly pure *l*-epicamphor is 5·5 grams.

d-*Bornylene-3-hydroxamic Acid*, $C_8H_{14}<\begin{matrix}C\cdot C(OH){:}N\cdot OH\\ \| \\ CH\end{matrix}$.

After a long series of comparative experiments the best conditions for the preparation of this acid—a process which is also the

* Epicamphor is appreciably volatile with ether, and therefore the ether distilled from solutions of this substance was always carefully kept and used for subsequent extractions.

first step in the preparation of epicamphor (p. 2206)—appear to be the following.* Hydroxylamine hydrochloride (15 grams) is dissolved in hot methyl alcohol (100 c.c.), and, after cooling, mixed with a solution of sodium (4·6 grams) in methyl alcohol (60 c.c.). Methyl bornylene-3-carboxylate (39·2 grams) is then added, together with a solution of sodium (5 grams) in methyl alcohol (60 c.c.). After remaining over night in a cool place, during which crystals of the sodium salt of bornylene-3-hydroxamic acid (see below) frequently separate, the whole is heated in a thermostat at 50° for two days. The product (*A*) is rendered just acid by the addition of acetic acid, and mixed with excess of a concentrated solution of copper acetate, when a pale green, voluminous precipitate separates, which is collected, washed with water, drained on porous porcelain, and then dried at 60°. The powdered salt is covered with ether, saturated with hydrogen sulphide, at first in the cold and then at the boiling point; the filtrate and ether washings of the copper sulphide are evaporated, and the syrupy residue left over sulphuric acid in a vacuum desiccator until it crystallises, which it quickly does if it is rubbed from time to time. The nearly solid mass is left in contact with porous porcelain until free from oily impurity, and the colourless residue recrystallised from benzene, from which it separates as a voluminous mass of colourless, microscopic, hexagonal plates:

0·1243 gave 0·3077 CO_2 and 0·0954 H_2O. C=67·5; H=8·5.

0·1334 gave 8·5 c.c. N_2 at 16° and 761 mm. N=7·4.

$C_{11}H_{17}O_2N$ requires C=67·7; H=8·7; N=7·2 per cent.

d-*Bornylene-3-hydroxamic acid* melts at 136°, and is readily soluble in alcohol, ether, or hot benzene, sparingly so in cold benzene, light petroleum, or cold water, but it dissolves readily in hot water. The aqueous solution gives, on the addition of ferric chloride, an intense claret coloration. The *sodium* salt, obtained as described above, crystallises from methyl alcohol, in which it is comparatively sparingly soluble in the cold, in glistening prisms, which become opaque on exposure to the air, and the air-dry substance loses approximately 14·6 per cent. over phosphoric oxide under diminished pressure. When the salt is heated in the water-oven, it gradually decomposes, and swells up into threads, and, if heated in a capillary tube, the salt decomposes suddenly at about 105° and gives a white sublimate, which melts to a syrup at about 110°. If the experiment is carried out in a test-tube with about 0·1 gram of the salt, and the product of the decomposition is

* This process is modelled on the preparation of phenylpropionylhydroxamic acid (hydrocinnamylhydroxamic acid), recommended by Thiele and Pickard (*Annalen*, 1899, **309**, 197).

moistened with hydrochloric acid, diluted with water, and boiled, epicamphor distils with the steam, and crystallises on the cold part of the tube. Boiling with water also slowly decomposes the sodium salt, with the formation of epicamphor. When sulphuric acid is added to the dry salt an almost explosive decomposition occurs, and a white sublimate is formed. The sodium salt is very readily soluble in water, and yields, on the addition of hydrochloric acid, an immediate crystalline precipitate of the pure hydroxamic acid.

The Acetyl Derivative.—Bornylenehydroxamic acid dissolves gradually in twice its weight of pure acetic anhydride in the cold, and, after remaining for twenty-four hours, the product, on decomposition with water, yields a crystalline mass, which separates from benzene in hard prisms.

A still more convenient method of preparing this acetyl derivative is to moisten the sodium salt with acetic anhydride, and, after a few hours, to add water and purify the product by crystallisation from benzene:

0·1457 gave 0·3493 CO_2 and 0·1038 H_2O. C=65·4; H=7·9.
0·1569 „ 8·3 c.c. N_2 at 15° and 758 mm. N=6·1.
$C_{13}H_{19}O_3N$ requires C=65·8; H=8·0; N=5·9 per cent.

Acetylbornylene-3-hydroxamic acid melts at 115—116°, and is readily soluble in alcohol, ether, chloroform, or hot benzene, but it is comparatively sparingly soluble in cold benzene. It is very sparingly soluble in cold light petroleum, but separates well from the boiling solvent (b. p. 70—80°) in microscopic prisms. When the acetyl derivative is heated, it begins to decompose, with evolution of gas, at about 140°; decomposition is rapid at 150° and at higher temperatures an oil distils which, when boiled with hydrochloric acid, yields epicamphor. When the solution of the sodium salt of bornylenehydroxamic acid was shaken with a slight excess of benzoyl chloride and a little sodium hydroxide, a thick gum was produced, which, after extraction with ether and thoroughly washing, crystallised. The substance separated from a mixture of benzene and light petroleum in colourless crusts, melted at about 135°, and was doubtless the *benzoyl* derivative of the hydroxamic acid:

0·1962 gave 8·4 c.c. N_2 at 18·6° and 761 mm. N=4·9.
$C_{18}H_{21}O_3N$ requires N=4·7 per cent.

On dry distillation this benzoyl derivative gives a pungent smelling oil, which when boiled with dilute hydrochloric acid develops the odour of epicamphor.

The Formation and Preparation of l-*Epicamphor from* d-*Bornylene-3-hydroxamic Acid.*

I. *Formation of* l-*Epicamphor by the Action of Heat on* d-*Bornylene-3-hydroxamic Acid.*—In studying this curious decomposition bornylenehydroxamic acid (5 grams) was gradually heated in a sulphuric acid bath until it just commenced to melt, when vigorous decomposition set in, a pale yellow resin was formed, and at the same time ammonia was eliminated, and a strong odour of epicamphor also became apparent. The product was shaken with hydrochloric acid, and, after remaining for fifteen minutes, water was added, when a brown syrup separated, which soon became semi-solid. The whole was now distilled in steam, which carried over epicamphor and left only a small, brown, resinous residue; the distillate was extracted with ether, the ethereal solution shaken with sodium carbonate,* dried, and evaporated, when 3 grams of crude epicamphor remained, and, after contact with porous porcelain and without further purification, had α_D $-48{\cdot}1^\circ$. For the purpose of complete identification, the substance was converted into the oxime (m. p. 103°) and semicarbazone (m. p. 236—238°).

II. *Preparation of* l-*Epicamphor from* d-*Bornylene-3-hydroxamic Acid by the Agency of Toluene-*p*-sulphonyl Chloride.*—This process, which has been employed for the preparation of more than 400 grams of epicamphor, is, in its first stage, carried out much in the way already described in the case of the preparation of bornylene-3-hydroxamic acid (p. 2204), except that epicamphor appears to be produced in larger yield when a considerable excess of hydroxylamine and sodium methoxide is used. Hydroxylamine hydrochloride (21 grams), dissolved in methyl alcohol (150 c.c.), is mixed with methyl bornylene-3-carboxylate (40 grams), sodium (14 grams), dissolved in methyl alcohol (180 c.c.), is then gradually added, the temperature being kept below 20° during this operation. After remaining for twenty-four hours, the product is heated in a thermostat at 50° for two days, cooled, mixed with powdered ice, and then toluene-*p*-sulphonyl chloride (65 grams) added, and the whole vigorously shaken in a bottle on the machine for twelve hours continuously.

It is most important that the decomposition of the sodium salt of the hydroxamic acid by the sulphonyl chloride should be as complete as possible, and the shaking must therefore be very thorough, and as some heat is developed during the first two hours, care is taken to cool the bottle and release the pressure from time to time.

* On acidifying the sodium carbonate extract, 0·8 gram of crude bornylene-3-carboxylic acid separated and melted at 106—107°.

The product is mixed with water, and extracted twice with ether *; the ethereal solution is washed and evaporated, and the residue mixed with two volumes of hydrochloric acid and well shaken during half an hour; water is then added, and the whole distilled in steam, when crude epicamphor mixed with bornylenecarboxylic acid passes over as a semi-solid mass, which frequently chokes the condenser. Ether is distilled down the condenser, the distillate extracted with ether, and the ethereal solution evaporated: the residue is warmed with methyl-alcoholic potassium hydroxide (10 grams KOH) for an hour, water is then added, and the epicamphor, which separates as a solid, extracted with ether. The ethereal solution is washed very thoroughly, dried and evaporated, when a syrup remains, which, when stirred in a current of air, soon becomes nearly solid. After contact with porous porcelain, the epicamphor, which remains as a colourless solid, is sufficiently pure for all ordinary purposes. The porous porcelain from several such operations is extracted with ether in a Soxhlet apparatus, the extract evaporated and distilled under 100 mm. pressure, and, in this way, a considerable additional quantity of pure epicamphor is obtained.

The alkaline aqueous solution is evaporated until free from ether and methyl alcohol, acidified, and the nearly pure bornylene-3-carboxylic acid which separates is collected, washed, dried on porous porcelain, and employed in a subsequent operation.

The yields obtained in this preparation vary in a manner which is difficult to explain, but, if the operation is successful, the result should be about as follows:

Epicamphor, obtained directly	14	grams.
,, recovered from plates by distillation	5	,,
Recovered bornylenecarboxylic acid	6 9	,,

The yield of epicamphor, allowing for the recovered bornylenecarboxylic acid, is therefore nearly 76 per cent. of that theoretically possible. It may be further purified by conversion into the semicarbazone (p. 2209) and subsequent regeneration by means of hydrochloric acid:

0·2145 gave 0·6151 CO_2 and 0·2062 H_2O. C=78·2; H=10·7.
0·1975 ,, 0·5693 CO_2 ,, 0·1876 H_2O. C=78·6; H=10·6.
$C_{10}H_{16}O$ requires C=79·0; H=10·5 per cent.

During the purification of the crude epicamphor by distillation in steam, as described above, the liquid remaining in the steam distillation flask generally deposits colourless crystals on keeping, sometimes in considerable quantity.

These were collected and recrystallised from dilute hydrochloric

* See footnote, p. 2203.

acid, from which the substance separated in glistening plates melting at 135—137°. On investigation this substance was recognised as toluene-*p*-sulphonamide, $CH_3\cdot C_6H_4\cdot SO_2\cdot NH_2$ (Found, C=49·9; H=5·3; N=8·2. $C_7H_9O_2S$ requires C=49·1; H=5·3; N=8·2 per cent.), and it is remarkable that this amide should be sufficiently stable to survive the long-continued distillation with dilute hydrochloric acid.

The Properties and Derivatives of l-*Epicamphor.*

l-Epicamphor melts at about 182° and distils at 213° (camphor melts at 177—178° and distils at 207°), and has a penetrating odour closely resembling and yet distinct from that of *d*-camphor. It is sparingly soluble in water, but readily so in alcohol or ether, and when placed on water it rotates like camphor. It is very readily volatile in steam. *l*-Epicamphor is lævorotatory, the value at 19° in benzene solution at a concentration of 13·1205 being α_D −58·21°, whereas camphor, under similar conditions, has α_D +39·1°. On reduction, *l*-epicamphor is converted into *l*-epiborneol (p. 2222), but it is comparatively stable to oxidising agents and is scarcely attacked by cold dilute permanganate or when boiled with dilute nitric acid (D 1·25), but more concentrated acid gradually attacks it, with formation of *d*-camphoric acid. In carrying out this oxidation, epicamphor (1 gram) was heated with nitric acid (13 c.c. of D 1·3) in a sealed tube for three hours at 100°, and then for a further three hours at 115°, when, on keeping, a crystalline substance separated, and a further quantity was obtained by evaporting the acid liquid and rubbing the semi-solid residue with chloroform. The substance was recrystallised from water, and shown to be camphoric acid by the fact that it melted at 186°, yielded an anhydride melting at 222—224°, and that mixtures of these substances with ordinary camphoric acid and its anhydride exhibited no alteration in their melting points. As was to be expected, the camphoric acid obtained by the oxidation of epicamphor showed exactly the same dextrorotation as a specimen prepared from ordinary camphor.

l-*Epicamphoroxime*, $C_8H_{14}<\begin{matrix}C:N\cdot OH\\ |\\ CH_2\end{matrix}$, may be obtained by adding sodium ethoxide and hydroxylamine hydrochloride to the alcoholic solution of *l*-epicamphor, but it is more conveniently prepared, and in almost quantitative yield, by the following process. Epicamphor (5 grams), hydroxylamine hydrochloride (4 grams), and excess of sodium acetate are digested with alcohol for an hour. On adding water, the milky liquid soon crystallises, and, after collecting, washing with water, and drying on porous porcelain, the oxime

melts at 98—100°, and is almost pure. It separates from dilute methyl alcohol at first as a milky precipitate, but this on stirring at once crystallises in glistening needles:

0·1398 gave 0·3710 CO_2 and 0·1315 H_2O. C=72·3; H=10·4.
0·2238 „ 16·8 c.c. N_2 at 22° and 760 mm. N=8·6.
0·1397 „ 10·8 c.c. N_2 „ 25° „ 758 mm. N=8·5.
$C_{10}H_{17}ON$ requires C=71·8; H=10·2; N=8·4 per cent.

Epicamphoroxime melts at 103—104°, is very readily soluble in the usual organic solvents, and has the odour of mice so characteristic of camphoroxime. It is dextrorotatory, the solution of 0·6293 gram, made up to 10 c.c. in benzene, having α_D +100·5°. Camphoroxime is lævorotatory, the solution of 0·5196 gram, made up to 10 c.c. in benzene, having α_D −56·0°.

l-*Epicamphorsemicarbazone*, $C_8H_{14}{<}{\begin{matrix}C{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2\\ |\\ CH_2\end{matrix}}$.—In order to prepare this derivative, *l*-epicamphor (7·7 grams), dissolved in alcohol, was mixed with a solution of semicarbazide hydrochloride (6·5 grams) and crystallised sodium acetate (8 grams) in water (20 grams), and boiled for one and a-half hours on the steam-bath, and then left over-night, during which the bulk of the semicarbazone (8·3 grams) had crystallised, and a further quantity (1·4 grams) was precipitated from the alcoholic solution by the addition of water. The substance was purified by recrystallisation from alcohol, from which it separated in microscopic, flat needles, which are quite different in appearance from the short prisms of camphorsemicarbazone:

0·1483 gave 0·3444 CO_2 and 0·1239 H_2O. C=63·3; H=9·3.
0·1039 „ 19 c.c. N_2 at 22° and 760 mm. N=20·7.
$C_{11}H_{19}ON_3$ requires C=63·2; H=9·1; N=20·1 per cent.

When rapidly heated, epicamphorsemicarbazone melts and decomposes at 237—238° (camphorsemicarbazone melts and decomposes at 247—248°); it is very sparingly soluble in water, but dissolves readily in hot methyl or ethyl alcohol. It dissolves in concentrated hydrochloric acid, and, if the solution is at once diluted with water, part separates unchanged, but when the whole is distilled in steam, the unchanged substance dissolves, decomposition rapidly takes place, and pure epicamphor distils over.

Bromo-l-epicamphor, $C_8H_{14}{<}{\begin{matrix}CO\\ |\\ CHBr\end{matrix}}$.—In order to prepare this substance, epicamphor (3 grams) was mixed in a tube with bromine (3·5 grams) and heated in the steam-bath for two hours. The crystalline product which separated was collected, dissolved in ether, in which it is not very readily soluble, the ethereal solution washed with dilute sodium hydroxide, dried and evaporated, and the pale

brown, crystalline mass left in contact with porous porcelain until quite dry. The substance was then dissolved in light petroleum (b. p. 50–60°), and the solution concentrated, when, on cooling, groups of needles crystallised, but when the solution was allowed to concentrate spontaneously the substance separated in glistening elongated prisms. The mother liquors were carefully examined, and yielded a further quantity of the same substance, but there was no evidence of the presence of any isomeride:

0·1488 gave 0·1198 AgBr. Br = 34·2.

$C_{10}H_{15}OBr$ requires Br = 34·6 per cent.

Bromo-l-*epicamphor* melts at 133—134° (bromocamphor at 76°), and dissolves readily in chloroform or benzene, but less so in alcohol; it is rather sparingly soluble in cold light petroleum, and much more readily so on warming:

0·7242, dissolved in ethyl acetate and made up to 20 c.c., had α_D −86·6°, whereas the rotation of bromocamphor in 10 per cent. alcoholic solution is α_D +140°.

Behaviour of l-*Epicamphor in Contact with Hydrocyanic Acid.*

For reasons stated in the introduction (p. 2191), the behaviour of epicamphor in contact with hydrocyanic acid was investigated under various conditions, but in no case could any signs of combination be observed; thus, in one experiment, finely-divided epicamphor (2 grams) was shaken in a stoppered bottle with pure potassium cyanide (5 grams) dissolved in a little water, and made nearly acid by the addition of acetic acid. The epicamphor liquefied, and, after twenty-four hours, the whole was extracted with ether, the ethereal solution dried and evaporated, when a solid residue of epicamphor was left, and almost the whole was recovered in this way, so that, if any combination had taken place, it must have been to a very slight extent.

The iso*Nitroso*-l-*epicamphors and Amino*-l-*epicamphor.*

The two (α- and β-) *iso*nitroso-*l*-epicamphors are obtained together by the action of sodamide and *iso*amyl nitrite on the ethereal solution of epicamphor under the following conditions (P., 1912, **28**, 57).

Epicamphor (10 grams), dissolved in anhydrous ether (100 c.c.), is mixed with finely-powdered sodamide (4 grams), and, after two hours, freshly distilled *iso*amyl nitrite (9 c.c.) is gradually added, the temperature being kept at 0° during the addition. After remaining for twenty-four hours at the ordinary temperature, the orange-red solution is mixed with ice-water, the ethereal layer

separated, and the aqueous solution once more extracted with ether; it is then freed from ether by passing a stream of air, and acidified with acetic acid, when an oil separates in quantity, and gradually solidifies. The solid (8·5 grams) was collected, left in contact with porous porcelain over sulphuric acid in a vacuum desiccator, and then dissolved in hot light petroleum (b. p. 80—85°) with the addition of a little benzene, when, on keeping, groups of long needles separated first, and these were rapidly collected and purified by repeated recrystallisation from the same solvent:

0·1363 gave 0·3320 CO_2 and 0·1022 H_2O. C=66·4; H=8·3.
0·1156 „ 8·0 c.c. N_2 at 19° and 750 mm. N=7·8.
$C_{10}H_{15}O_2N$ requires C=66·2; H=8·3; N=7·7 per cent.

α-isoNitroso-l-epicamphor melts at 168—170°, and dissolves readily in warm alcohol, benzene, or chloroform, and it differs from the β-modification (see below) by being much more sparingly soluble in light petroleum. It dissolves readily in dilute sodium hydroxide with a pale yellow colour, and when the solution is acidified with acetic acid it may remain clear for some time, and then gradually deposits crystals of the pure α-modification. A solution containing 0·799 in benzene, made up to 20 c.c., gave α_D −201·9°. Forster and Spinner, who obtained α-*iso*nitrosoepicamphor by another process (T., 1912, **101**, 1350), found the melting point to be 170° and the rotation, in chloroform, α_D −200·1°. They also prepared the benzoyl derivative (m. p. 122·5°, α_D −128·7°), the *O*-methyl ether (m. p. 100°, α_D −201·5°), and the phenylurethane (m. p. 106°, α_D −110·2°).

α-*iso*Nitroso-*l*-epicamphor dissolves readily in a 40 per cent. formaldehyde solution, and if, after heating on the steam-bath for an hour, hydrochloric acid is added and the solution boiled, it at once turns yellow and deposits crystals of camphorquinone. Concentrated sulphuric acid dissolves α-*iso*nitrosoepicamphor, and the solution, heated on the steam-bath for two or three minutes and then diluted with water, yields a white, crystalline precipitate, which, after recrystallisation, melts at 244—245°, and consists of the imide of *d*-camphoric acid.

β-isoNitroso-l-epicamphor.—The light petroleum mother liquors from the crystallisation of the α-derivative yielded, on slow evaporation, a small crop of crystals, which consisted of a mixture of the α- and β-isomerides, and then pale yellow prisms of the almost pure β-derivative. These were collected and further purified by fractional crystallisation from light petroleum:

0·1453 gave 0·3526 CO_2 and 0·1091 H_2O. C=66·2; H=8·4.
0·1722 „ 12·1 c.c. N_2 at 18° and 752 mm. N=8·0.
$C_{10}H_{15}O_2N$ requires C=66·2; H=8·3; N=7·7 per cent.

β-iso*Nitroso*-l-*epicamphor* melts at 138—140°, and dissolves readily in alcohol, benzene, chloroform, or light petroleum, and is also moderately soluble in boiling water. Rotation: 1·0138 dissolved in benzene and made up to 20 c.c., gave α_D −183·5°. Forster and Spinner (T., 1912, **101**, 1349) also found that this substance melts at 140°, and they give the rotation for the solution in chloroform as −179·4°, rising to −191·4° in seven days. β-*iso*Nitroso-*l*-epicamphor is converted into the α-isomeride by heating above its melting point or when its solution in water is boiled. It yields camphorquinone on treatment with formaldehyde and then with hydrochloric acid, and the imide of camphoric acid when it is heated with concentrated sulphuric acid (Claisen and Manasse, *Annalen*, 1893, **274**, 73). The benzoyl derivative (m. p. 8?°, α_D −130·0°), the *O*-methyl ether (m. p. 77°, α_D −173·6°), and the phenylurethane (m. p. 118°, α_D −124·3°) have been prepared by Forster and Spinner (*loc. cit.*, pp. 1349—1350).

Amino-l-*epicamphor*, $C_8H_{14}<\begin{smallmatrix}CO\\|\\CH\cdot NH_2\end{smallmatrix}$, is produced by the reduction either of α- or β-*iso*nitrosoepicamphor by means of zinc dust and aqueous alkali. The *iso*nitrosoepicamphor (10 grams) is dissolved in sodium hydroxide (40 c.c. of 30 per cent.), and then zinc dust (12 grams) added in small quantities at a time, when the deep yellow colour of the solution almost completely disappears. The oily precipitate is extracted with ether, the ethereal solution dried over potassium carbonate, evaporated, and the thick syrup, which has a penetrating and most unpleasant odour, is stirred until it has completely crystallised. The mass is left in contact with porous porcelain, and then recrystallised by dissolving it in boiling light petroleum (b. p. 45—50°), and then cooling in a freezing mixture, and, since it becomes viscid and decomposes on heating, it was dried in a current of air free from carbon dioxide:

0·1425 gave 0·3749 CO_2 and 0·1281 H_2O. C=71·7; H=10·0.

0·1917 „ 13·9 c.c. N_2 at 18° and 761 mm. N=8·3.

$C_{10}H_{17}ON$ requires C=71·8; H=10·2; N=8·4 per cent.

Amino-l-*epicamphor* melts at 168—170°, and is readily soluble in alcohol, ether, benzene, or light petroleum, and also in water; the solution of 0·5902 in benzene, made up to 10 c.c., gave α_D +15·0°.

Forster and Spinner (*loc. cit.*, p. 1355) found that aminoepicamphor melted at 168—169°, and, in alcoholic solution, had α_D +11·9°. We have not noticed that aminoepicamphor changes so rapidly as these authors seem to suggest, and specimens which have been sealed up for a year seem hardly to have altered in appearance. The discrepancy in the rotations (α_D +30·15° instead

f -15·07°; compare P., 1912, **28**, 57) which Forster and Spinner ..m to think may have been due to partial change of the substance ..to epidihydrodicamphenepyrazine, was in reality due to a mistake 1 our calculation, the volume of the benzene solution having been ..ken as 20 c.c. instead of 10 c.c. We can confirm the statement f Forster and Spinner that the α- and β-*iso*nitroso-*l*-epicamphors ..th yield the same amino-*l*-epicamphor on reduction, and, there..re, in most of our experiments, the isomeric *iso*nitroso-derivatives ..ere not first separated, but the mixture was directly used for the ..duction.

l-*Epicamphorcarboxylic Acid*, $C_8H_{14}<\overset{CO}{\underset{CH\cdot CO_2H}{|}}$.

The first specimens of this acid were prepared by a method ..ilar to that recommended for the preparation of camphorcarb..ylic acid (Brühl, *Ber.*, 1891, **24**, 3384; compare Bredt, *Annalen*, ..09, **366**, 11), namely, by acting on sodium *l*-epicamphor with ..rbon dioxide. Thin sodium ribbon (2·2 grams) was covered ..th a solution of epicamphor (10 grams) in absolute ether (120 c.c.) .. a double-necked flask, fitted with a very efficient condenser and ..tube for the delivery of carbon dioxide, and heated on the steam..th whilst a rapid stream of carbon dioxide was passed. The ..action commences at once, and, if care is taken not to let it ..acken, the sodium will, at the end of two to three hours, have been ..most completely used up; the mass is then allowed to remain ..er-night, and the heating and passage of carbon dioxide continued ..r another hour. The product is decomposed by ice, the aqueous ..lution separated, extracted with ether, and carefully concentrated .. the steam-bath, when, on fractionally precipitating with dilute ..drochloric acid, a resinous substance first separates, and, after ..moving this by filtration, almost pure epicamphorcarboxylic acid ..parates on the further addition of the hydrochloric acid, but the ..ld is not more than 2 grams. The ethereal solution, on evapora..on, deposited 5·1 grams of a solid, and from this, on distillation .. steam, 2 grams of a substance was obtained, which melted at ..–179°, and consisted of *l*-epiborneol (p. 2222) mixed with a ..tle epicamphor. The portion not volatile in steam contains a ..bstance which crystallises from light petroleum in slender needles, ..elts at 256—257°, and is probably the pinacone of *l*-epicamphor, ..ce it yielded the following results on analysis:

..·1657 gave 0·4743 CO_2 and 0·1683 H_2O. C=78·1; H=11·3.

$(C_{10}H_{17}O)_2$ requires C=78·4; H=11·2 per cent.

Other crystalline substances of lower melting point were also ..esent, the nature of which could not be determined.

Since the yield of epicamphorcarboxylic acid obtained by the above process was seldom more than 20 per cent. of that theoretically possible, and this loss of valuable epicamphor was serious, a long series of experiments was made first with the object of improving the method of preparation of camphorcarboxylic acid, and of then applying the process to epicamphor and with excellent results, since it is now possible to prepare epicamphorcarboxylic acid in a yield of at least 90 per cent. of that theoretically possible. The process consists in treating epicamphor with sodamide and carbon dioxide, but in benzene solution, since the reaction does not proceed with a satisfactory yield when ether is employed as the solvent.* Epicamphor (20 grams), dissolved in benzene (150 c.c.), is mixed with finely-powdered sodamide (14 grams) and heated to boiling in a two-necked flask connected with a condenser, and a rapid stream of carbon dioxide is passed through a tube which must be fitted with a wide end in order to avoid stoppage by the thick, gelatinous mass which rapidly forms. After about an hour the product is mixed with ice and water, the benzene solution separated, and the aqueous layer filtered and acidified with hydrochloric acid, when epicamphorcarboxylic acid separates in an almost pure condition, and a small quantity of less pure acid is obtained by extraction with ether. The benzene solution containing the unchanged epicamphor, and the amount of which may be approximately calculated from the weight of epicamphorcarboxylic acid resulting from the first operation, is thoroughly dried, half the benzene is removed by careful fractionation with a Young column, and the remaining solution again treated with sodamide and carbon dioxide, and the process is repeated until no more epicamphor remains in the benzene, and in this way an almost quantitative yield of epicamphorcarboxylic acid has been obtained on several occasions. The acid may be purified by contact with porous porcelain and recrystallisation from a mixture of benzene and light petroleum, from which it separates in colourless needles, but the best method is to dissolve the acid in a slight excess of sodium carbonate in a beaker fitted with a mechanical stirrer, and then to add very dilute hydrochloric acid until the small quantity of sticky impurity has been removed; after filtering, the acid obtained as a colourless precipitate on the addition of excess of hydrochloric acid is pure:

0·1937 gave 0·4473 CO_2 and 0·1444 H_2O. C = 67·4; H = 8·3.
0·1741 „ 0·4295 CO_2 „ 0·1295 H_2O. C = 67·3; H = 8·3
$C_{11}H_{16}O_3$ requires C = 67·3; H = 8·2 per cent.

l-*Epicamphorcarboxylic acid* is rather sparingly soluble in cold

* This process may be employed with equal success in the preparation of camphorcarboxylic acid.

water, but dissolves easily in alcohol, ether, or benzene, less readily in light petroleum. Owing to the fact that this acid, like camphorcarboxylic acid, is readily decomposed on heating with elimination of carbon dioxide, the melting point is difficult to determine. The behaviour of both acids was observed on the same thermometer, when epicamphorcarboxylic acid melted at 120—122°, camphorcarboxylic acid at 125—126°. In both cases decomposition took place on slowly raising the temperature, until the contents of the capillary tubes solidified to very pure epicamphor and camphor, which then melted sharply at 184—184·5° and 178—179° respectively.

Rotation of l-*Epicamphor Carboxylic Acid:* 0·7775, dissolved in ethyl acetate and made up to 20 c.c., gave α_D −18·5°; the rotation of *d*-camphorcarboxylic acid determined for the sake of comparison gave: 1·1615, dissolved in ethyl acetate and made up to 20 c.c., gave α_D +37·4°.

Oxidation to Camphoric Acid.—In order to determine the position of the carboxyl group in *l*-epicamphorcarboxylic acid (compare p. 2192) a small quantity of this acid was dissolved in sodium carbonate and oxidised by permanganate.

Camphorcarboxylic acid, under these conditions, yields camphorquinone as well as camphoric acid, and epicamphorcarboxylic acid might be expected to exhibit the same behaviour, but the formation of camphorquinone could not be observed. When the oxidation was complete, the alkaline filtrate from the manganese precipitate was evaporated to a small bulk and acidified, when camphoric acid separated and was identified by the melting point (186°) and the melting point of the anhydride (222°).

a-Bromo-l-*epicamphorcarboxylic Acid*, $C_8H_{14}<\begin{matrix}CO \\ | \\ CHBr\cdot CO_2H\end{matrix}$.—This substance is readily prepared by heating epicamphorcarboxylic acid (0·5 gram), dissolved in glacial acetic acid (5 c.c.) with bromine (0·5 gram) in a sealed tube in the water-bath. The change is a gradual one, but is complete in about four hours; the product is then mixed with two volumes of water, and allowed to remain for twenty-four hours. The bromo-acid which will have been deposited is collected, dissolved in dilute sodium carbonate, the solution filtered and acidified, when a voluminous mass of microcrystalline stars separate, which are collected, washed with water, and dried over phosphoric oxide:

0·1902 gave 0·1233 AgBr. Br = 29·1.

$C_{11}H_{15}O_3Br$ requires Br = 29·1 per cent.

a-Bromo-l-*epicamphorcarboxylic acid* melts, if rapidly heated, at about 145° with evolution of carbon dioxide, but it decomposes

at a considerably lower temperature if the determination is slowly carried out (α-bromocamphorcarboxylic acid melts at 112—113°). It is very sparingly soluble in water, more readily so in alcohol, and the alcoholic solution gives no coloration on the addition of ferric chloride.

When this bromo-acid is heated at 150° until the elimination of carbon dioxide is complete, a crystalline substance remains, which separates from light petroleum in plates, melts at 132—134°, and is identical with the bromo-*l*-epicamphor obtained by the direct bromination of epicamphor (p. 2210), since a mixture of the two substances melted at the same temperature as the components.

The l-*Epiborneolcarboxylic Acids*, $C_8H_{14}<\begin{matrix}CH\cdot OH\\ |\\ CH\cdot CO_2H\end{matrix}$.

It is well known that camphorcarboxylic acid cannot be reduced by sodium amalgam under the usual conditions, and, assuming this fact to be due to the proximity of the tertiary carbon atom to the CO-group, it seemed possible that epicamphorcarboxylic acid, in which the CO-group is not attached to a tertiary carbon atom might behave quite normally, and be readily reduced on treatment with sodium amalgam. *l*-Epicamphorcarboxylic acid (5 grams) was therefore dissolved in dilute sodium carbonate and shaken on the machine with a large excess of sodium amalgam for several hours, the alkaline solution was then decanted from the mercury, acidified, and distilled in steam, when a quantity of epicamphor passed over, showing that a good deal of the epicamphorcarboxylic acid had remained unchanged. When the residue from the steam distillation was extracted with ether, the ethereal solution left, on evaporation, only a small quantity (0·6 gram) of a gum which possibly contained epiborneolcarboxylic acids, but it is evident that epicamphorcarboxylic acid, like camphorcarboxylic acid, cannot be effectively reduced under these conditions. The acid is, however, readily reduced by means of potassium amalgam produced electrolytically in an apparatus similar to that recommended by Bredt (*J. pr. Chem.*, 1911, [ii], **84**, 792) for the reduction of camphorcarboxylic acid. The aqueous layer from this reduction of about 60 grams of epicamphorcarboxylic acid was nearly neutralised with hydrochloric acid, filtered, and then acidified, when a chalky precipitate separated, which was collected and left in contact with porous porcelain until quite dry. This represented practically the whole of the product, since ether extracted only about 2 grams from the filtrate. The chalky mass was carefully extracted with several quantities of boiling light petroleum (b. p. 80—100°) until an acid remained which melted at 168—172°. This was then twice crystallised from

...ing toluene, from which it separated as a voluminous mass of ... plates, and, when dry, had a beautiful, satiny appearance. [The] pure acid, which weighed 2·5 grams, melted at 173°, and is [c]alled (C)-l-*epiborneolcarboxylic acid*; the analysis and rotation of [th]e acid are given below. The mother liquors from this acid were [free]d from solvent by distillation from the steam-bath under [red]uced pressure, the mass was dissolved in sodium carbonate, the [ac]id again precipitated, dried, and extracted with boiling light [pe]troleum (b. p. 60—70°) until the residue melted at 140—145°, [and] this, which we propose to name (B)-l-*epiborneolcarboxylic acid*, [we]ighed 21·5 grams, and was the principal product of the reduc[t]ion.

The light petroleum mother liquors were exposed to the air and [a]llowed to concentrate spontaneously, when they next deposited ... grams of curious, warty nodules melting at 120—122°, and [the]se were collected and again crystallised by solution in light [pe]troleum and spontaneous concentration, when the melting point [ro]se to 125°, and was not altered by further crystallisation. This [ac]id is called (A)-l-*epiborneolcarboxylic acid*. The combined light [p]etroleum mother liquors were now allowed to concentrate very [s]lowly in the ice-chest, and yielded 1·5 grams of an acid which [s]oftened at 230° and melted at 237°, and it is curious that this [ac]id, although apparently the least soluble of all the isomerides, [s]hould separate after the others. This acid, for which the name (D)-l-*epiborneolcarboxylic acid* is proposed, was recrystallised from [li]ght petroleum, from which it separated in warty groups melting [a]t 237° with decomposition and slight previous softening. The [fi]nal mother liquors were evaporated, and yielded a mixture of the [e]piborneolcarboxylic acids, which were not separated by fractional [c]rystallisation, but used directly for the preparation of bornylene-2-[c]arboxylic acid (p. 2218).

Analyses and rotations of the epiborneolcarboxylic acids:

(A)-l-*Epiborneolcarboxylic Acid*, m. p. 125°.

0·1110 gave 0·2700 CO_2 and 0·0910 H_2O. C=66·4; H=9·1.

$C_{11}H_{18}O_3$ requires C=66·7; H=9·1 per cent.

0·9299, dissolved in ethyl acetate and made up to 20 c.c., gave α_D +2·36°.

(B)-l-*Epiborneolcarboxylic Acid*, m. p. 145°.

0·1224 gave 0·2985 CO_2 and 0·1004 H_2O. C=66·4; H=9·1.

1·1046, dissolved in ethyl acetate and made up to 20 c.c., gave α_D −4·8°.

(C)-l-*Epiborneolcarboxylic Acid*, m. p. 173°.

0·1175 gave 0·2865 CO_2 and 0·0952 H_2O. C=66·5; H=9·0.

0·2174, dissolved in ethyl acetate and made up to 20 c.c., gave α_D +15·18°.

(D)-l-*Epiborneolcarboxylic acid* melts at 237° with evolution of gas, but without darkening, and the melted mass did not crystallise on cooling. It is almost insoluble in hot water, but dissolves readily in alcohol, boiling light petroleum (b. p. 90—100°), or in boiling toluene:

0·1452 gave 0·3555 CO_2 and 0·1134 H_2O. C=66·8; H=8·7.
0·1306 ,, 0·3201 CO_2 ,, 0·1028 H_2O. C=66·7; H=8·7.
0·1386, dissolved in ethyl acetate and made up to 20 c.c., had α_D +77·9°.

$C_{11}H_{18}O_3$ requires C=66·7; H=9·1 per cent.
$C_{22}H_{34}O_6$ requires C=67·0; H=8·6 per cent. (compare p. 2193).

All the epiborneolcarboxylic acids are stable to permanganate, that is to say, their solutions in a slight excess of sodium carbonate mixed with ice do not decolorise permanganate on keeping for about a minute, and the most readily oxidisable of the isomerides appears to be the (A)-acid.

l-*Bornylene-2-carboxylic Acid*, $C_8H_{14}<\begin{matrix}CH\\ \Vert\\ C\cdot CO_2H\end{matrix}$, *and* l-*Camphane-2-carboxylic Acid*, $C_8H_{14}<\begin{matrix}CH_2\\ \vert\\ CH\cdot CO_2H\end{matrix}$.

In preparing *l*-bornylene-2-carboxylic acid, the crude mixture of *l*-epiborneolcarboxylic acids (p. 2216, 30 grams) was mixed with acetyl chloride (150 c.c.) and heated to boiling in a reflux apparatus for fifteen hours; the excess of acetyl chloride was then distilled off, and the syrupy mass distilled under diminished pressure (15 mm.), when almost the whole passed over, and only a small crystalline residue remained.

The syrupy distillate and the residue were dissolved in methyl alcohol (200 c.c.) and sulphuric acid (15 c.c.), and, after remaining over-night, the whole was heated in a reflux apparatus for one hour; water was then added, and the oily methyl ester extracted with ether.

The ethereal solution was well washed with sodium carbonate, dried, evaporated, and the oil twice distilled under diminished pressure, when almost the whole quantity passed over at 155°/100 mm.:

0·1668 gave 0·4533 CO_2 and 0·1410 H_2O. C=74·1; H=9·4.
$C_{12}H_{18}O_2$ requires C=74·2; H=9·3 per cent.

0·6596, dissolved in ethyl acetate and made up to 20 c.c., gave α_D −95·7°, but this value must not be taken as the true rotation of this methyl ester.

The methyl l-*bornylene-2-carboxylate* thus obtained (25 grams) was hydrolysed by boiling for an hour with methyl-alcoholic potassium hydroxide (KOH = 20 grams); water was added, the solution nearly neutralised with hydrochloric acid, and the methyl alcohol removed by evaporation. When the filtered solution was acidified, a syrup separated, which soon crystallised, and, after remaining in contact with porous porcelain until dry, the acid was further purified by recrystallisation from dilute acetone or formic acid, or it may be distilled in steam, with which, however, it passes over somewhat slowly:

0·1386 gave 0·3715 CO_2 and 0·1107 H_2O. C = 73·1; H = 8·9.
0·1471 „ 0·3922 CO_2 „ 0·1166 H_2O. C = 72·7; H = 8·9.
$C_{11}H_{16}O_2$ requires C = 73·3; H = 8·9 per cent.

0·5161, dissolved in ethyl acetate and made up to 20 c.c., gave α_D −98·82°.*

l-*Bornylene-2-carboxylic acid* melts at 115°, and is readily soluble in alcohol, benzene, light petroleum, ether, or acetic acid, but very sparingly so in water, and crystallises from dilute acetic acid in irregular plates.

The solution of the sodium salt decolorises permanganate, although not instantaneously.

Oxidation.—*l*-Bornylene-2-carboxylic acid is quickly oxidised by nitric acid, and, in studying this oxidation, the pure acid (0·5 gram) was warmed with nitric acid (25 c.c. of D 1·24) in a reflux apparatus, when a vigorous reaction set in, and some of the acid distilled with the nitric acid and crystallised in the condenser. After boiling for an hour a further quantity (15 c.c.) of the same acid was added, and the boiling continued for twelve hours; the product was then repeatedly evaporated with the addition of water, and the crystalline mass extracted with chloroform. The residue separated from water in glistening plates melting at 185°, and, on titration, 0·0891 neutralised 9·03 c.c. $N/10$-NaOH, whereas this amount of a dibasic acid, $C_{10}H_{16}O_4$, should neutralise 8·94 c.c. $N/10$-NaOH. Since the acid yielded an anhydride melting at 216—218°, there can be no doubt that it was d-*camphoric acid*.

l-*Camphane-2-carboxylic Acid*.—This acid is readily obtained by reducing bornylene-2-carboxylic acid, in dilute methyl-alcoholic solution, with hydrogen in the presence of palladium and gum arabic under the conditions already described in the case of the corresponding reduction of bornylene-3-carboxylic acid to camphane-3 carboxylic acid (p. 2199).

The product was distilled in steam, the distillate made alkaline

* The rotation of *d*-bornylene-3-carboxylic acid, in benzene solution, at a concentration of 13·1506 is α_D + 149·5°.

with sodium carbonate, evaporated until free from methyl alcohol, mixed with powdered ice and a little permanganate, and allowed to remain for an hour, but the addition of hydrogen had evidently been practically complete, since there was hardly any reduction of the permanganate.

After the removal of the permanganate, the acid was precipitated by hydrochloric acid, washed well, and dried on porous porcelain.

Owing to the fact that it is so very soluble in the usual organic solvents, the recrystallisation of this acid is a matter of difficulty, and the best plan seems to be to dissolve it in warm dilute acetic acid, and then to cool the solution below 0°, when the pure acid separates well in long, colourless needles, which are collected on a filter surrounded by a freezing mixture:

0·1343 gave 0·3560 CO_2 and 0·1198 H_2O. C=72·3; H=9·9.

$C_{11}H_{18}O_2$ requires C=72·5; H=9·9 per cent.

0·7489, dissolved in ethyl acetate and made up to 20 c.c., gave α_D −37·8°.

l-Camphane-2-carboxylic acid melts at 78—80°, and distils at about 155°/15 mm.; it is very sparingly soluble in cold, but dissolves somewhat in boiling water, and separates, on cooling, in glistening needles.

It is mentioned on p. 2194 that this acid had already been prepared by Houben and Kesselkaul (*Ber.*, 1902, **35**, 3696; compare Houben, *Ber.*, 1905, **38**, 3799), who named it "hydropinenecarboxylic acid," and state that it melts at 72—74°, and by Zelinsky (*Ber.*, 1902, **35**, 4417), who gives the melting point 69—71°, and called it "camphanecarboxylic acid."

Conversion of l*-Bornylene-2-carboxylic Acid into* d*-Camphor.*

The interesting conversion of *l*-bornylene-2-carboxylic acid—and indirectly of epicamphor—into camphor was brought about through the agency of *l*-bornylene-2-hydroxamic acid (compare p. 2206). Hydroxylamine hydrochloride (12 grams), carefully dried and powdered, was dissolved in anhydrous methyl alcohol (100 c.c.), and mixed in the cold with a solution of sodium (3·5 grams) in methyl alcohol. Methyl *l*-bornylene-2-carboxylate (30 grams) was then added, and afterwards sodium (3·5 grams) dissolved in methyl alcohol (50 c.c.), and the whole allowed to remain for two days, during which no crystallisation of the sodium salt of the hydroxamic acid took place. After heating for four hours in a thermostat at 50° the product was divided into the halves (A) and (B). The portion (A) was mixed with water, a small quantity of unchanged ester (1·5 grams) extracted with ether, the aqueous solution was just acidified with hydrochloric acid and extracted three times with ether, and,

after washing well, drying, and evaporating carefully, the ethereal solution deposited a syrup which did not crystallise. This syrupy acid, which gave an intense claret coloration when ferric chloride was added to its alcoholic solution, was dissolved in a slight excess of potassium hydroxide, and the pale blue copper salt precipitated by the addition of excess of copper acetate; the precipitate was washed, dried, suspended in ether, and decomposed by hydrogen sulphide. After filtering, the ethereal solution yielded, on evaporation, an almost colourless syrup, which did not crystallise even after several days' exposure over sulphuric acid, but analysis indicated that this syrup was practically pure l-*bornylene-2-hydroxamic acid*:

0·1180 gave 9·1 c.c. N_2 at 17° and 755 mm. N = 7·2.
$C_{11}H_{17}ON_2$ requires N = 7·2 per cent.

Conversion of l-*Bornylene-2-hydroxamic Acid into* d-*Camphor by Heat.*—This conversion was brought about by heating the syrupy hydroxamic acid in a reflux apparatus at about 120°, when decomposition commenced and continued, after the flame had been removed, so vigorously that the temperature rose to about 200°; a good deal of ammonia was formed, and some camphor crystallised in the neck of the flask and in the condenser. The product was mixed with concentrated hydrochloric acid and distilled in steam, and the semi-solid mass, which smelt strongly of camphor, was extracted with ether. The ethereal solution yielded, on evaporation, a buttery mass, which was left for some hours in contact with methyl-alcoholic potassium hydroxide (KOH = 5 grams) *; water was then added, and the crystalline precipitate extracted with ether.

After washing thoroughly, the ethereal solution was dried and carefully evaporated, when a nearly solid mass remained, which, in contact with porous porcelain, became quite dry, and consisted of nearly pure *d*-camphor, a fact which was proved by recrystallising it from a little very light petroleum (b. p. 35—40°), when it melted at 174—176°, had α_D +46·9° in ethyl acetate solution, and yielded camphoroxime melting at 119°.

Conversion of l-*Bornylene-2-hydroxamic Acid into* d-*Camphor with the Aid of Toluene*-p-*sulphonyl Chloride.*—The second portion (B) of the solution of the sodium salt of *l*-bornylene-2-hydroxamic acid, obtained as described above, was mixed with twice its volume of water, and shaken for twelve hours on the machine with finely-powdered toluene-*p*-sulphonyl chloride (25 grams). The product was extracted with ether, the ethereal solution washed, dried, and

* The alkaline solution, after the methyl alcohol has been removed by evaporation, yielded, on acidifying, crude bornylene-2-carboxylic acid (2 grams).

evaporated, and shaken for half an hour with concentrated hydrochloric acid. Water was then added, and the whole distilled in steam, when a semi-solid mass passed over, and a brown button and some crystals containing nitrogen and sulphur were left in the distillation flask (compare p. 2208). The distillate was extracted with ether, the ethereal solution evaporated, and the residual crude camphor mixed with methyl-alcoholic potassium hydroxide (5 grams KOH) and warmed on the steam-bath for half an hour in order to hydrolyse some bornylene-2-carboxylic ester which was present. Water was then added, the camphor extracted with ether, the ethereal solution very thoroughly washed, dried, and evaporated, and the *d*-camphor left on porous porcelain until quite dry, and then twice recrystallised from light petroleum (b. p. 30—40°). It was then quite pure, since it melted at 176°, and, when treated with hydroxylamine under the conditions given on p. 2208, yielded camphoroxime melting at 119°. Furthermore, there was no alteration in melting point when these preparations were mixed with ordinary *d*-camphor, which had been recrystallised from light petroleum, and with *d*-camphoroxime. The determination of the rotation gave the following result: 0·4002, dissolved in ethyl acetate and made up to 20 c.c., gave α_D +47·7°, whereas the rotation of ordinary *d*-camphor, after crystallisation from light petroleum, was α_D +48·0° under the same conditions.

The yield of camphor obtained in the above experiment was more than 40 per cent. of that theoretically possible.

$$\text{l-}\textit{Epiborneol},\ C_8H_{14}{<}\begin{matrix}CH\cdot OH\\ |\\ CH_2\end{matrix}.$$

In order to obtain this substance, *l*-epicamphor, dissolved in ten times its weight of ethyl alcohol, was reduced, in a reflux apparatus, with an equal weight of sodium, which was added as rapidly as possible in order that the whole might pass into solution. If any sodium remains it is removed by the addition of ice; the whole is then distilled in steam, when the epiborneol passes over much in the same way, but not so readily, as epicamphor, and a considerable portion solidifies in the condenser, and must be removed from time to time by solution in ether.

The ethereal solution is combined with the ether extract of the distillate, washed thoroughly with water to remove the alcohol, dried, and evaporated, when l-*epiborneol* remains as a crystalline mass, which melts at 179—181°, and, after purification with the aid of the phenylurethane, at 181—182·5°:

0·1550 gave 0·4415 CO_2 and 0·1695 H_2O. C=77·7; H=12·2.
0·1392 „ 0·3975 CO_2 „ 0·1495 H_2O. C=77·8; H=11·9.
$C_{10}H_{18}O$ requires C=77·9; H=11·7 per cent.

It is remarkable that all the specimens of *l*-epiborneol which we have obtained have proved to be inactive.

The *phenylurethane*, $C_{10}H_{17}\cdot O\cdot CO\cdot NH\cdot C_6H_5$, was prepared by dissolving epiborneol (6 grams) in a little light petroleum (b. p. 35—40°), adding phenylcarbimide (5 grams), and allowing the mixture to remain for several days in a sealed tube, during which some of the phenylurethane separated in white crystals, and the addition of more light petroleum precipitated a further quantity of the same substance:

0·1607 gave 0·4402 CO_2 and 0·1238 H_2O. C=74·7; H=8·6.
0·1910 „ 9·4 c.c. N_2 at 17·5° and 733·5 mm. N=5·5.
$C_{17}H_{23}O_2N$ requires C=74·7; H=8·5; N=5·1 per cent.

l-*Epibornylphenylurethane* separates from light petroleum in groups of long needles, and melts at 82°; it is readily decomposed by distillation with dilute hydrochloric acid, and pure epiborneol passes over with the condensed water.

Preparation of l-*Epiborneol from Sodium* l-*Epibornylxanthate.*

When sodium epibornylxanthate (see below) is dissolved in hot water and mixed with hydrochloric acid a precipitate of epiborneol is at once produced, and, after distilling in steam, extracting with ether, and evaporating, the solid was recrystallised from light petroleum several times, but the melting point remained constant at 176—176·5°, whereas the substance obtained from *l*-epicamphor by reduction with sodium and alcohol had melted at 181—182·5°:

0·1822 gave 0·5176 CO_2 and 0·191 H_2O. C=77·5; H=11·7.
$C_{10}H_{18}O$ requires C=77·9; H=11·7 per cent.

It was at first thought that these two substances were stereoisomeric, and corresponded with borneol and *iso*borneol, which, as is well known, occur together in the product of the reduction of camphor. That this is probably not the case is indicated by the fact that both preparations were inactive, and that, in spite of the difference in melting points, both gave the same phenylurethane.

Conversion of l-*Epiborneol into* l-*Bornylene by the Method of Tschugaev.*

This interesting conversion of inactive *l*-epiborneol into active *l*-bornylene was carried out under the following conditions: In the first place, sodium epibornylxanthate was prepared by adding sodium ribbon (3 grams) to the solution of *l*-epiborneol (15 grams)

in absolute ether (150 c.c.) in a flask protected from moisture and carbon dioxide by a calcium chloride and soda-lime tube, when a slow and regular evolution of hydrogen set in, and was complete after remaining over-night. The unchanged sodium ribbon was easily removed, and the solution of sodium borneol was then mixed with carbon disulphide (15 grams), when a yellow precipitate separated immediately and the contents of the flask became nearly solid. The precipitate of sodium *l*-epibornylxanthate was collected and recrystallised from water, when about 70 per cent. separated as a very pale yellow, almost white, crystalline mass, and, from the mother liquors, epiborneol was recovered by treatment with hydrochloric acid. The sodium salt was converted into methyl *l*-epibornylxanthate, $C_8H_{14}<\begin{matrix}CH\cdot O\cdot CS_2Me\\ |\\ CH_2\end{matrix}$, by suspending it in ether, adding methyl iodide, and boiling in a reflux apparatus, the whole being repeatedly shaken to ensure complete decomposition. After ten hours the product was mixed with water, the ethereal solution dried and evaporated, when the methyl ester remained as a rather mobile, yellow oil.

This oil was now heated in a small distillation flask by means of a small flame, and the gases evolved (methyl mercaptan and carbonyl sulphide) ignited, so that the progress of the decomposition could be judged by the size of the jet. After a short time bornylene commenced to distil over, and crystallised in the receiver as a colourless mass. The distillation was repeated, and the *l*-bornylene then distilled over sodium, when it melted sharply at 113—114°, but did not exhibit constant rotation, since different portions of the distillate had values varying between α_D $-16\cdot93°$ and $-19\cdot58°$. After a further distillation over sodium, the solution of two different specimens in benzene gave the values:

Melting point.	Concentration.	α_D.
113—114°	4·771	−18·45°
114·5—115	4·345	−18·41

Oxidation.—In carrying out this experiment, the above *l*-bornylene (2 grams) was dissolved in benzene and shaken with 700 c.c. of 1 per cent. permanganate on the machine for twenty hours; the excess of permanganate was then decomposed by sulphur dioxide, and the filtrate and washings from the manganese precipitate concentrated, acidified, and the precipitated acid extracted with ether. After distilling off the ether, the mass was boiled with chloroform, decanted, and the residue recrystallised from water, when an acid was obtained, which melted at 188°, and proved on examination to consist of pure *d*-camphoric acid.

l-Bornylene had been previously obtained by Bredt (*Annalen*,

1909, **366**, 52) by the decomposition of sodium β-bromodihydrobornylene-3-carboxylate (compare p. 2191), and was found to have the constants: m. p. 113°; b. p. 146°; rotation, in toluene solution at a concentration of 10·45, α_D −21·69°. More recently, Tschugaev and Budrick (*Annalen*, 1912, **388**, 288) prepared *d*-bornylene from methyl *l*-bornylxanthate (from *l*-borneol) by heating at 176—177°, and this specimen melted at 109—109·5°, distilled at 146·5°/750 mm., and, in toluene solution at a concentration of 12·75, had α_D +19·29°.

On oxidation with permanganate it yielded *l*-camphoric acid.

ORGANIC LABORATORY OF THE KÖNIGL. TECHNISCHEN HOCHSCHULE-AACHEN.

THE UNIVERSITIES OF OXFORD AND MANCHESTER.

CCXXXII.—*Synthesis of* d- *and* l-*Sylvestrene.*

By WALTER NORMAN HAWORTH and WILLIAM HENRY PERKIN, jun.

d-SYLVESTRENE—that important terpene which Atterberg discovered in Swedish oil of turpentine in 1877 (*Ber.*, **10**, 1202; 1878, **11**, 1698), and which Baeyer (*Ber.*, 1894, **27**, 3488; 1898, **31**, 1067) first showed to be a derivative of *m*-cymene—is isolated from the Swedish oil in the form of the dihydrochloride, a highly characteristic derivative which melts at 72° and has α_D +22·6°. The constitution of this dihydrochloride has been proved to be that represented by the formula:

$$CH_2{<}\begin{matrix}CMeCl\cdot CH_2\\CH_2\text{—}CH_2\end{matrix}{>}CH\cdot CMe_2Cl$$

(compare this vol., p. 1230), and *d*-sylvestrene is prepared by heating it with substances, such as diethylaniline, which serve to remove two molecules of hydrogen chloride. In a recent communication (this vol., p. 1232), Haworth, Perkin, and Wallach have shown that the terpene thus obtained is not a single substance, but is probably a mixture mainly of the Δ^1- and Δ^6-isomerides:

$$\underset{\Delta^1.}{CH_2{<}\begin{matrix}CMe{=}CH\\CH_2\cdot CH_2\end{matrix}{>}CH\cdot CMe{:}CH_2} \quad \text{and} \quad \underset{\Delta^6.}{CH{\ll}\begin{matrix}CMe\cdot CH_2\\CH_2\text{—}CH_2\end{matrix}{>}CH\cdot CMe{:}CH_2}$$

elimination of hydrogen chloride within the ring taking place in two directions, and there is also reason to believe that other isomeric substances, of the terpinolene class, are present in small quantity.

l-Sylvestrene is practically unknown, since the only mention of

this substance appears in a paper by A. More (T., 1899, 75, 718), who, by distilling the oil obtained from the oleo-resin of *Dacrydium hexandra*, obtained a lævorotatory oil which distilled at 173—176°, and yielded a dihydrochloride melting at 71°; its rotation was not determined, but it exhibited the characteristic crystalline form of sylvestrene dihydrochloride. Unfortunately, the amount of material available was insufficient for further investigation.

dl-Sylvestrene (carvestrene) was first prepared by Baeyer (*Ber.*, 1894, **27**, 3486; compare also *Ber.*, 1898, **31**, 1402; and T., 1907, **91**, 481) from carone by conversion into vestrylamine, the hydrochloride of which decomposes, on distillation, into ammonium chloride and carvestrene, a process which Baeyer represented thus:

$$CH_2\left<\begin{matrix}CHMe\cdot CH(NH_2)\\ CH_2\text{———}CH_2\end{matrix}\right>CH\cdot CMe{:}CH_2 \longrightarrow$$

Vestrylamine.

$$CH_2\left<\begin{matrix}CMe{=}CH\\ CH_2\cdot CH_2\end{matrix}\right>CH\cdot CMe{:}CH_2$$

Carvestrene.

During the course of a series of experiments, made with the object of synthesising sylvestrene and its derivatives, the first positive result was the synthesis of *dl*-sylvestrene (T., 1907, **91**, 482), by a long process of which, for the purposes of the present communication, it will be necessary to call attention only to the following stages.

The ester of *cyclo*hexanone-3-carboxylic acid is converted by treatment with magnesium methyl iodide into 1-methyl*cyclo*hexan-1-ol-3-carboxylic acid:

$$CH_2\left<\begin{matrix}CO{-}CH_2\\ CH_2\cdot CH_2\end{matrix}\right>CH\cdot CO_2H \longrightarrow CH_2\left<\begin{matrix}C(OH)Me\cdot CH_2\\ CH_2\text{———}CH_2\end{matrix}\right>CH\cdot CO_2H,$$

from which, by the action of hydrobromic acid, 1-bromo-1-methyl-*cyclo*hexane-3-carboxylic acid was obtained, and this, when heated with pyridine, was decomposed, with elimination of hydrogen bromide and formation of 1-methyl-Δ^1-*cyclo*hexene-3-carboxylic acid:

$$CH_2\left<\begin{matrix}CMeBr\cdot CH_2\\ CH_2{-}{-}CH_2\end{matrix}\right>CH\cdot CO_2H \longrightarrow CH_2\left<\begin{matrix}CMe{=}CH\\ CH_2\cdot CH_2\end{matrix}\right>CH\cdot CO_2H.$$

That the acid of this constitution was formed was proved conclusively by the fact that adipic acid was obtained on oxidation, and at that time it was thought that the elimination of hydrogen bromide had taken place entirely in the direction of the carboxyl group, and that the unsaturated acid did not contain any of the Δ^6-isomeride:

$$CH\left<\begin{matrix}CMe\cdot CH_2\\ CH_2{-}CH_2\end{matrix}\right>CH\cdot CO_2H.$$

The next development was the synthesis of *d*-sylvestrene, and the first step in this was the resolution of the acid, obtained in the manner described above, by means of brucine, when an acid was obtained which had α_D +90·8°, and subsequently +108°, and this was assumed to be pure *d*-1-methyl-Δ^1-*cyclo*hexenecarboxylic acid (P., 1910, **26**, 97).*

When the ester of this acid was treated with magnesium methyl iodide, it yielded a *d*-dihydrocarvestrenol (*d*-sylveterpineol), which was thought to be pure *d*-Δ^1-*m*-menthenol(8), and this, on treatment with hydrochloric acid, was converted into *d*-sylvestrene dihydrochloride, which melted at 72°, had α_D +22·5°, and was identical in all respects with a specimen of the dihydrochloride which had been prepared from Swedish oil of turpentine.

When this dihydrochloride was decomposed by diethylaniline, it yielded a specimen of *d*-sylvestrene, which distilled at 174—176°, and had α_D +67·5°, and thus the synthesis of *d*-sylvestrene was accomplished.

The most remarkable characteristic of the *d*-sylveterpineol obtained as the result of the above series of reactions was the fact that the first specimen was apparently without rotation, but a second specimen, which Prof. Pope kindly examined, had the small lævorotation α_D −2·7°.

When the acid, recovered from the mother liquors of the brucine salt of the acid of α_D +108°, was systematically treated with *l*-menthylamine, an acid of rotation α_D −49·7° was ultimately separated.

The ester of this acid was prepared, and yielded, on treatment with magnesium methyl iodide in the usual manner, an *l*-sylveterpineol, which had α_D −45·9°, and this, in contact with hydrochloric acid, was converted into a dihydrochloride, which melted at 72°, had α_D −22·1°, and was therefore obviously l-*sylvestrene dihydrochloride*. When this dihydrochloride was treated with diethylaniline, it yielded l-*sylvestrene*, which distilled at 175—178° and had α_D −66·5°, and in this way the synthesis of *l*-sylvestrene was accomplished. It was also interesting to observe that, when equal weights of *d*- and *l*-sylvestrene dihydrochlorides were mixed and the product recrystallised from methyl alcohol, the crystals which separated melted sharply at 52°, and consisted of pure carvestrene dihydrochloride.

The experiments which have just been described make it quite clear that the acid obtained by the elimination of hydrogen bromide from 1-bromo-1-methyl*cyclo*hexane-3-carboxylic acid (com-

* By an unfortunate mistake in the calculation, the rotation of this acid is erroneously given here as α_D +70°.

pare 2226) could not have been a single substance, but must have consisted of a mixture of *dl*-acids, the rotations of the active constituents of which are approximately represented by the values α_D 108° and 49·7°, and of these the latter was always present in by far the larger quantity. Since both of these acids ultimately lead to sylvestrene dihydrochloride, it is obvious that the one must be 1-methyl-Δ^1-*cyclo*hexene-3-carboxylic acid, and the other the corresponding Δ^6-isomeride, and the possibility of the formation of these from the bromo-acid is clear from the following scheme:

$$CH_2{<}\begin{matrix}CMeBr{\cdot}CH_2\\CH_2{-}{-}CH_2\end{matrix}{>}CH{\cdot}CO_2H \quad \begin{matrix}\nearrow CH_2{<}\begin{matrix}CMe{:}CH\\CH_2{\cdot}CH_2\end{matrix}{>}CH{\cdot}CO_2H\\ \searrow CH{\lessdot}\begin{matrix}CMe{\cdot}CH_2\\CH_2{-}CH_2\end{matrix}{>}CH{\cdot}CO_2H\end{matrix}$$

In order to discover which of these acids corresponded with the rotation α_D 108° and which with that of α_D 49·7°, the following series of experiments was undertaken. 1-Methyl-Δ^6-*cyclo*hexene-3-carboxylic acid had been prepared by Fisher and Perkin (T., 1908, **93**, 1878) by another series of reactions, namely, from 1-methyl*cyclo*hexan-6-one-3-carboxylic acid, by reduction, conversion into the bromo-acid and subsequent elimination of hydrogen bromide:

$$CO{<}\begin{matrix}CHMe{\cdot}CH_2\\CH_2{-}{-}CH_2\end{matrix}{>}CH{\cdot}CO_2H \rightarrow CH(OH){<}\begin{matrix}CHMe{\cdot}CH_2\\CH_2{-}{-}CH_2\end{matrix}{>}CH{\cdot}CO_2H \rightarrow$$

$$CHBr{<}\begin{matrix}CHMe{\cdot}CH_2\\CH_2{-}{-}CH_2\end{matrix}{>}CH{\cdot}CO_2H \rightarrow CH{\lessdot}\begin{matrix}CMe{\cdot}CH_2\\CH_2{-}CH_2\end{matrix}{>}CH{\cdot}CO_2H,$$

and it seemed probable at the time, not only that the acid obtained had this constitution, but that it was free from the Δ^5-isomeride:

$$CH{\lessdot}\begin{matrix}CHMe{\cdot}CH_2\\CH_2{-}{-}CH_2\end{matrix}{>}CH{\cdot}CO_2H,$$

which might conceivably have been produced during the above process of preparation. In the present communication (p. 2230) oxidation experiments are described which clearly demonstrate these points. A large quantity of this acid (210 grams) was prepared and resolved by means of brucine and *l*-menthylamine, and, after an unusually laborious series of fractional crystallisations, the *d*-acid was obtained with the rotation α_D +108°, and the *l*-acid with α_D −98·6°. When the ester of the *d*-acid was treated with magnesium methyl iodide, it yielded *d*-Δ^6-*m*-menthenol(8), which had the small lævorotation α_D −2·7°, and, in contact with hydrochloric acid, was converted into *d*-sylvestrene dihydrochloride, which melted at 72°, and had α_D +22·5°, and this, on

treatment with diethylaniline, gave a specimen of *d*-sylvestrene, which distilled at 175—178°, and had $\alpha_D + 67.5°$.

A similar series of experiments with the *l*-acid of rotation $\alpha_D - 98.6°$ gave *l*-sylvestrene dihydrochloride (m. p. 70—72°; $\alpha_D - 21.8°$), and from this, *l*-sylvestrene, boiling at 176—178° and having $\alpha_D - 68.2°$, was isolated. It is thus conclusively proved that the rotation α_D 108° is the characteristic of 1-methyl-Δ^6-*cyclo*hexene-3-carboxylic acid, and therefore that the rotation of the Δ^1-acid must be represented approximately by the value α_D 49.7°.

If further proof were necessary, it was obtained by submitting the acid of rotation $\alpha_D - 49.7°$ to oxidation, when it yielded adipic acid (p. 2236).

The *l*-Δ^1-acid yielded a *l*-Δ^1-*m*-menthenol(8), which exhibited the rotation $-45.9°$, a value which, except that it is of opposite sign, is identical with that observed in the case of a specimen of sylveterpineol which had been obtained by the action of potassium hydroxide on *d*-sylvestrene dihydrochloride (this vol., p. 1234). But there can be little doubt that the *d*-sylveterpineol obtained from the dihydrochloride in this way contains a certain, although probably small, quantity of *d*-Δ^6-*m*-menthenol(8):

$$CH{<}{\begin{matrix}CMe\cdot CH_2\\ CH_2-CH_2\end{matrix}}{>}CH\cdot CMe_2\cdot OH,$$

and, as it is shown in the present communication that the *d*-Δ^6-isomeride has a slight lævorotation of about $\alpha_D - 2.7°$, its presence must reduce the rotation of the *d*-Δ^1-isomeride, the true value of which is therefore probably somewhat higher than $\alpha_D + 45.9°$.

It was pointed out on another occasion (T., 1911, **99**, 559) that, probably owing to their feebly acidic properties and to the tendency of the constituents of their salts with active bases to separate from solvents as isomorphous mixtures or mixed crystals, the resolution of the *cyclo*hexene acids is a most laborious process, and the operations described in the present communication required more than two years to complete. It was therefore found impossible to carry the resolution of the Δ^1-acid to a further stage, and this, although no doubt desirable, was actually not necessary, since the acids obtained were readily converted into optically pure specimens of *d*- and *l*-sylvestrene and their hydrochlorides.

EXPERIMENTAL.

Oxidation of dl-1-*Methyl*-Δ^6-cyclo*hexene*-3-*carboxylic Acid.*

In the previous paper describing this acid (T., 1908, **93**, 1885) no definite proof was offered that the acid obtained, and also used

in the present research, did actually contain the double linking in the Δ^6-position. In order to supply this proof, the acid was oxidised with ozone and then with permanganate and hypobromite under the following conditions: Ozonised oxygen was first passed through the solution of the acid (10 grams) in sodium carbonate until it was no longer absorbed, and the solution was then treated with permanganate at 0° until the pink colour remained for five minutes. The filtrate and washings from the manganese precipitate were evaporated to a small bulk, acidified, and extracted several times with ether on the machine, when a large yield of a syrupy acid was obtained, which, since it showed no signs of crystallising, was completely esterified by digesting with alcohol (70 c.c.) and sulphuric acid (5 c.c.) in a reflux apparatus for five hours. Water was then added, the ester extracted with ether, the ethereal solution thoroughly washed with water and dilute sodium carbonate, dried, evaporated, and distilled, when about 20 per cent. passed over below 170° and the remainder constantly at 175°/18 mm.

The following analysis agreed with the formula

$$Me\cdot CO\cdot CH_2\cdot CH(CO_2Et)\cdot CH_2\cdot CH_2\cdot CO_2Et:$$

0·1189 gave 0·2567 CO_2 and 0·0910 H_2O. C=58·9; H=8·6.
$C_{12}H_{20}O_5$ requires C=59·0; H=8·2 per cent.

This ester was digested with dilute hydrochloric acid (5 per cent.) for ten hours; the whole was then evaporated to complete dryness by distillation from the water-bath under a pressure of 15 mm., and the nearly colourless syrup left over powdered potassium hydroxide in a vacuum desiccator and constantly stirred until it contained only a trace of hydrochloric acid. This substance yielded the following analytical results, agreeing with the formula

$$Me\cdot CO\cdot CH_2\cdot CH(CO_2H)\cdot CH_2\cdot CH_2\cdot CO_2H:$$

0·1446 gave 0·2389 CO_2 and 0·0845 H_2O. C=50·7; H=6·5.
$C_8H_{12}O_5$ requires C=51·1; H=6·4 per cent.

Titration: 0·4142 requires, for neutralisation, 44·9 c.c. N/10-NaOH, whereas this amount of a dibasic acid, $C_8H_{12}O_5$, should neutralise 44·1 c.c. N/10-NaOH.

Oxidation of the Acid, $C_8H_{12}O_5$, *by means of Sodium Hypobromite.*—In this experiment sodium hydroxide (8 grams), dissolved in water (50 c.c.) and powdered ice (about 100 grams), was gradually mixed with bromine (10 grams), and then the solution of the dibasic acid, $C_8H_{12}O_5$ (7·5 grams), in a slight excess of sodium hydroxide was rapidly added with vigorous mechanical stirring. In a short time the separation of bromoform was complete, and after remaining for an hour, the bromoform (about 3 grams) was run off, the solution acidified with sulphuric and sulphurous acids,

saturated with ammonium sulphate, and extracted five times with much ether on the machine. The well-dried ethereal solution deposited, on evaporation, a syrup which gradually crystallised, and, after remaining in contact with porous porcelain until quite dry, the acid was recrystallised from acetone, from which it separated in lustrous prisms:

0·1307 gave 0·2116 CO_2 and 0·0634 H_2O. C=44·1; H=5·4.

$C_7H_{10}O_6$ requires C=44·2; H=5·3 per cent.

That this acid, which melted at 117—118°, was butane-$\alpha\beta\delta$-tricarboxylic acid, $CO_2H\cdot CH_2\cdot CH(CO_2H)\cdot CH_2\cdot CH_2\cdot CO_2H$, was confirmed by the fact that, when it was mixed with a specimen of this acid which had previously been obtained synthetically by Kay and Perkin (T., 1906, **89**, 1644), there was no alteration in melting point. It is therefore clear that the product of the oxidation of the unsaturated acid by ozone and permanganate is *hexan-ε-one-αγ-dicarboxylic acid*,

$$Me\cdot CO\cdot CH_2\cdot CH(CO_2H)\cdot CH_2\cdot CH_2\cdot CO_2H,$$

and the formation of this acid proves that the *dl*-acid employed in this series of oxidations is *dl*-1-methyl-Δ^6-*cyclo*hexene-3-carboxylic acid. The porous porcelain which had been employed in the purification of the crude butanetricarboxylic acid was extracted with ether in a Soxhlet apparatus, and the small quantity of syrupy acid dissolved in a little concentrated hydrochloric acid and allowed to remain over powdered potassium hydroxide for some days with frequent stirring, when it deposited a further small quantity of the same acid, and there was no evidence of the presence of any other substance.

Resolution of dl-1-*Methyl*-Δ^6-cyclo*hexene*-3-*carboxylic Acid*,

$$CH{<}^{CMe\cdot CH_2}_{CH_2-CH_2}{>}CH\cdot CO_2H.$$

Several active bases were employed in the preliminary experiments on the resolution of this acid, but ultimately advantage was more particularly taken of the brucine salts and the salts with *l*-menthylamine, and, as illustrations of the methods employed, the following experiments only will be described in detail:

I.—*Isolation of* d-1-*Methyl*-Δ^6-cyclo*hexene*-3-*carboxylic Acid by means of Brucine. Method* I.—The *dl*-acid (50 grams), dissolved in ethyl acetate, was mixed with rather more than half the quantity of brucine required for neutralisation (75 grams), dissolved in ethyl acetate, the solution was then well shaken with small quantities of water until a few drops remained undissolved,* and

* In all these resolutions it was found that, whereas the brucine salts crystallise with difficulty and then very imperfectly from dry ethyl acetate, the crystallisation is much facilitated when the solvent is saturated with water.

allowed to remain in the ice-chest, when a thick crust of crystals soon separated, and these were collected and four times recrystallised from ethyl acetate. The salt was then decomposed by sodium carbonate, the brucine collected, washed, and the alkaline solution concentrated, acidified, and extracted with ether, when 5 grams of acid were obtained, which, after distillation, had α_D +59·7°.*

Method II.—The *dl-acid* (14 grams) was exactly neutralised with N/10-sodium hydroxide, heated to boiling, and then an alcoholic solution containing brucine (60 grams) and the *dl*-acid (14 grams) was added, and the whole evaporated nearly to dryness. When the syrupy residue was vigorously stirred with water, crystallisation was gradually induced, and, after remaining in the ice-chest for several days, the pasty mass was transferred to the pump, washed with a little ice water, and dissolved in boiling water, in which it was readily soluble. The felted mass of needles, which separated on cooling, was several times recrystallised from water, during which operation it was noticed that the salt became gradually less soluble and more granular in appearance.

The salt was then decomposed in the usual manner, and yielded 3·5 grams of an acid which distilled at 138—140°/18 mm., and had α_D +108°, and as, in a subsequent experiment, more frequent crystallisation of the brucine salt did not produce any rise in the rotation, it is assumed that α_D +108° is the true rotation of *d*-1-methyl-Δ^6-*cyclo*hexene-3-carboxylic acid.

II.—*Isolation of* l-1-*Methyl*-Δ^6-cyclo*hexene*-3-*carboxylic Acid by means of* l-*Menthylamine*.—After the brucine salt of the *d*-acid had been removed as completely as possible by the repeated application of the methods just described, the acid was recovered from the mother liquors, distilled, and then systematically treated with *l*-menthylamine, and the following experiment may be described as an example of this treatment. The *l*-acid of rotation α_D −17·6° (50 grams) was dissolved in N-sodium hydroxide (365 c.c.), heated to boiling, and then a hot solution of *l*-menthylamine hydrochloride (75 grams) was added all at once with vigorous stirring, when an oily layer separated at the surface, and, on remaining in the ice-chest for a few days, this became a thick paste of crystals. The aqueous solution, after decanting and filtering, yielded about 7 grams of acid, which was nearly inactive, and the pasty menthylamine salt was left in contact with porous porcelain until quite dry. After twice recrystallising from methyl ethyl ketone, the salt yielded, on decomposition with sodium carbonate, an acid which, after distillation, had α_D −32·5°, and

* The concentration employed in all the determinations mentioned in this communication was roughly 5 per cent., and the solvent was always ethyl acetate.

by repeating this treatment with *l*-menthylamine a large number of times both with this acid of rotation $-32.5°$ and with the acid which was absorbed as *l*-menthylamine salt by the porous plates, a specimen (11 grams) of l-1-*methyl*-Δ^6-cyclo*hexene*-3-*carboxylic acid* was obtained, which had the rotation α_D $-98.6°$ instead of the rather higher value α_D $-108°$, which would correspond with the highest value observed in the case of the *d*-acid.

Synthesis of d- *and* l-*Sylvestrene.*

In the synthesis of *d*-sylvestrene, *d*-1-methyl-Δ^6-*cyclo*hexene-3-carboxylic acid (12 grams; α_D $+108°$) was converted into the ester by means of alcoholic sulphuric acid in the usual manner, and the ester was then added to an ethereal solution of magnesium methyl iodide containing 6 grams of magnesium. After remaining overnight, the product was decomposed by water and distilled in steam, the distillate was extracted with ether, the ethereal solution evaporated, and, in order to remove possible traces of unchanged ester, the oily residue was mixed with a solution of potassium hydroxide (3 grams) in methyl alcohol, and allowed to remain for twenty-four hours. After diluting with water, the pleasant-smelling oil was extracted with ether, the ethereal solution thoroughly washed, dried, and evaporated, and the *d*-Δ^6-*m*-menthenol(8) distilled, when the whole quantity passed over at 106—107°/20 mm., and, as far as could be observed in the apparatus at our disposal, appeared to have no rotation (compare P., 1910, **26**, 97). A second sample was subsequently prepared and sent to Prof. Pope, who was good enough to examine it in his more accurate instrument, and found that it was lævorotatory, although only to a slight extent. The results of his measurements are as follows:

3·3354 grams, made up to 20·05 c.c. with pure ether, gave the following values in a 2-dcm. tube at 19·5°:

α $-1.155°$ for mercury green, whence $[\alpha]_{gr}$ $-3.46°$.
α $-0.960°$ for mercury yellow, whence $[\alpha]_{ye}$ $-2.88°$.
α $-0.910°$ for sodium yellow, whence $[\alpha]_D$ $-2.73°$.

The purity of the sample was tested by an analysis which gave the following results:

0·1451 gave 0·4140 CO_2 and 0·1551 H_2O. C=77·8; H=11·9.
$C_{10}H_{18}O$ requires C=77·9; H=11·9 per cent.

When this d-Δ^6-m-*menthenol*(8) was left in contact with concentrated hydrochloric acid, crystallisation soon commenced, and, after remaining in the ice-chest for two days, the crystalline mass was transferred to porous porcelain and left over sulphuric acid until quite dry. The colourless residue then melted at 65—68°,

and, after once crystallising from methyl alcohol, from which it separated in brilliant leaflets, it melted sharply at 72°, had α_D +22·5°, and consisted of pure *d*-sylvestrene dihydrochloride, $C_{10}H_{16},2HCl$. The identity was established by analysis (Found, Cl=33·9. $C_{10}H_{18}Cl_2$ requires Cl=34·0 per cent.), and by the fact that, when mixed with a specimen of *d*-sylvestrene dihydrochloride from Swedish oil of turpentine, there was no alteration in melting point. In order to complete the synthesis of *d*-sylvestrene, the pure hydrochloride (7·5 grams) was decomposed by diethylaniline, the terpene distilled in steam, and, after extraction with ether, twice distilled over solid potassium hydroxide, when almost the whole quantity passed over at 175—178°, and had α_D +67·5°, d_{18} 0·8485, and n_D 1·4752, whence M=45·25 (calculated for $C_{10}H_{16}\overline{|}^{2}$ 45·24). These values agree almost exactly with those observed by Wallach (*Annalen*, 1888, **245**, 198) in the case of a specimen of *d*-sylvestrene which he had obtained by distilling pure sylvestrene dihydrochloride from Swedish oil of turpentine with aniline, and which distilled at 175—176° and had α_D +66·32° and n_D 1·4757. There can thus be no doubt that the synthetical terpene, obtained as described above, is identical with the *d*-sylvestrene of Swedish oil of turpentine.

Synthesis of l-*Sylvestrene*.—In order to carry out this synthesis, *l*-1-methyl-Δ^6-*cyclo*hexene-3-carboxylic acid (11 grams of α_D −98·6°; compare p. 2233) was converted into the methyl ester by treatment with methyl alcohol and sulphuric acid, and this, after isolation in the usual manner and without distillation, was mixed with an ethereal solution of magnesium methyl iodide containing 6 grams of magnesium.

The product was isolated in the manner already described in the case of the *d*-ester, and yielded 10 grams of *l*-Δ^6-*m*-menthenol(8), which distilled at 106—108°/21 mm., and had a slight dextrorotation of about α_D +1°. In contact with concentrated hydrochloric acid, this menthenol was rapidly converted into a crystalline mass, which separated from methyl alcohol in glistening leaflets, melted at 70—72°, and had α_D −21·8°. This l-*sylvestrene dihydrochloride* was decomposed by diethylaniline in the usual manner, and yielded l-*sylvestrene*, and, when this was twice carefully fractionated, the portion distilling at 176—178° had α_D −68·2°, d_{19} 0·848, and n_D 1·4761, whence M=45·24, whereas the value calculated for $C_{10}H_{16}\overline{|}^{2}$ is M=45·24.

The final experiment was to mix equal quantities (0·5 gram) of *d*- and *l*-sylvestrene dihydrochlorides, and to recrystallise the product from a small quantity of methyl alcohol, when a considerable crop of crystals was obtained which melted sharply at

52° and consisted of ***carvestrene dihydrochloride*** (*dl*-sylvestrene dihydrochloride).

Resolution of dl-1-*Methyl*-Δ^1-cyclo*hexene*-3-*carboxylic Acid*,

$$\mathrm{CH_2}\!<\!\begin{matrix}\mathrm{CMe\!:\!CH}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}\!>\!\mathrm{CH\cdot CO_2H}.$$

It is stated in the introduction that the acid employed in these experiments and obtained by the elimination of hydrogen bromide from 1-bromo-1-methyl*cyclo*hexan-3-carboxylic acid, is a mixture of *dl*-1-methyl-Δ^1- and *dl*-1-methyl-Δ^6-*cyclo*hexenecarboxylic acids:

$$\mathrm{CH_2}\!<\!\begin{matrix}\mathrm{CMeBr\cdot CH_2}\\ \mathrm{CH_2{-\!-}CH_2}\end{matrix}\!>\!\mathrm{CH\cdot CO_2H}\quad\begin{matrix}\nearrow & \mathrm{CH_2}\!<\!\begin{matrix}\mathrm{CMe\!:\!CH}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}\!>\!\mathrm{CH\cdot CO_2H}\quad \Delta^1.\\ \searrow & \mathrm{CH}\!\ll\!\begin{matrix}\mathrm{CMe\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}\!>\!\mathrm{CH\cdot CO_2H}\quad \Delta^6.\end{matrix}$$

and that this fact made the resolution and separation of the active constituents of the *dl*-Δ^1-acid a very difficult and laborious process, which necessitated the use of a large quantity (295 grams) of the mixed acids. The process can only be indicated by the following examples: The mixed acids (in quantities of 70 grams) were dissolved in a slight excess of $N/10$-sodium hydroxide (510 c.c.), heated nearly to boiling, and then a hot aqueous solution of *l*-menthylamine hydrochloride (100 grams) was poured in with constant stirring. The oily layer which separated remained syrupy for several days, but, when vigorously stirred and left in the ice-chest, it gradually crystallised.

After fourteen days the aqueous layer was decanted, and yielded, on acidifying, nearly inactive acid (9 grams); the buttery menthylamine salt was left in contact with porous porcelain until quite dry, and the residue rubbed to a stiff paste with methyl ethyl ketone and again transferred to porous porcelain. The salt, which weighed 94 grams, was then twice recrystallised from methyl ethyl ketone, when it had α_D $-34{\cdot}5°$ and yielded an acid of rotation α_D $-16{\cdot}3°$. The plates containing the more soluble *l*-menthylamine salt were extracted with ether in a Soxhlet apparatus, the acid recovered, distilled, and treated again in the same manner, except that only 75 per cent. of the required amount of *l*-menthylamine was employed, and, by systematically continuing this process, 78 grams of acid, which had α_D $-16{\cdot}5°$, were separated from the 295 grams of the original mixture of *dl*-acids.

When this was repeatedly treated with *l*-menthylamine, an acid (22 grams) was gradually collected, which had α_D $-49{\cdot}7°$, and it

was found that this consisted of approximately pure *l*-1-*methyl-Δ¹-*cyclo*hexene-3-carboxylic acid.*

In order to demonstrate this, the unsaturated acid (5 grams) was dissolved in sodium carbonate and treated with ozone until absorption no longer took place; the product was then oxidised with permanganate at 0° until the colour persisted for two minutes. After acidifying, saturating with ammonium sulphate, and repeatedly extracting with ether on the machine, a syrup was obtained, which yielded bromoform when it was treated with sodium hypobromite, and evidently consisted of impure hexane-one-α-carboxylic acid (acetylvaleric acid; compare T., 1890, 57, 230), $COMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, since, when it was digested with dilute nitric acid and the product evaporated to dryness under diminished pressure, crystals of adipic acid separated (compare T., 1907, **91**, 497).

The formation of adipic acid proves that the unsaturated acid of rotation α_D −49·7° must be 1-methyl-Δ¹-*cyclo*hexene-3-carboxylic acid:

$$CH_2<\begin{matrix}CMe{:}CH\\CH_2{\cdot}CH_2\end{matrix}>CH{\cdot}CO_2H \longrightarrow CH_2<\begin{matrix}CO{\cdot}Me\\CH_2{\cdot}CH_2\end{matrix}\diagup^{CH_2{\cdot}CO_2H}$$

$$\longrightarrow CO_2H{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H.$$

d-1-*Methyl*-Δ⁶-cyclo*hexene-3-carboxylic Acid.*—After the mixture of *dl*-1-methyl-Δ¹- and *dl*-1-methyl-Δ⁶-*cyclo*hexene-3-carboxylic acids had been exhaustively treated with *l*-menthylamine in the manner just described, the acid was recovered from the mother liquors, distilled, and then converted into the brucine salt by the process described under method II on p. 2232. The resulting syrupy mixture of brucine salts was mixed with a little water and vigorously stirred from time to time, when, after some weeks, it deposited a considerable quantity of crystals, which were collected, several times recrystallised from water, and the acid recovered. This acid after distillation had α_D +90·8°, and, although not optically pure (the rotation should have been α_D +108°, compare p. 2232), this was proved to consist mainly of *d*-1-methyl-Δ⁶-*cyclo*hexene-3-carboxylic acid, since, when converted into the methyl ester and this added to an ethereal solution of magnesium methyl iodide, it yielded *d*-Δ⁶-*m*-menthenol(8), which was almost inactive, and was converted into *d*-sylvestrene dihydrochloride (m. p. 72°; α_D +22·1°) by contact with concentrated hydrochloric acid.

This was indeed the first specimen of *d*-Δ⁶-*m*-menthenol(8) which was obtained, and which served for the first synthesis of *d*-sylvestrene, a preliminary description of which appeared in 1910 (P., **26**, 97). The mother liquors of the brucine salt of the *d*-Δ⁶-acid must have contained *d*-1-methyl-Δ¹-*cyclo*hexene-3-carboxylic acid and

1-methyl-Δ^6-*cyclo*hexene-3-carboxylic acid, but no attempt was made to isolate these active constituents.

Conversion of l-1-*Methyl*-Δ^1-cyclo*hexene*-3-*carboxylic Acid into* l-Δ^1-m-*Menthenol*(8) *and* l-*Sylvestrene.*

In this series of experiments, *l*-1-methyl-Δ^1-*cyclo*hexene-3-carboxylic acid of a_D $-49{\cdot}7°$ (12 grams) was dissolved in 10 per cent. methyl-alcoholic sulphuric acid (100 c.c.), and, after two days, the methyl ester was isolated in the usual manner and distilled, when it passed over at 144—147°/100 mm. This ester was gradually added to an ethereal solution of magnesium methyl iodide (containing 6 grams of magnesium), and, after remaining overnight, the product was decomposed by water and distilled in steam. The distillate was extracted with ether, the ethereal solution evaporated, and the residue left in contact with alcoholic potassium hydroxide (KOH = 3 grams) for twenty-four hours; water was then added, and the menthenol again extracted and distilled:

0·1318 gave 0·3771 CO_2 and 0·1402 H_2O. C = 77·8; H = 11·8.

$C_{10}H_{18}O$ requires C = 77·9; H = 11·7 per cent.

The l-Δ^1-m-*menthenol*(8) thus obtained distilled at 106—108°/20 mm., and had a_D $-45{\cdot}9°$, but this rotation, for reasons given on p. 2229, is probably somewhat lower than the true value. This menthenol gradually combines with hydrogen chloride, but not so readily as Δ^6-*m*-menthenol(8) does, and, in contact with porous porcelain, the semi-solid product left a colourless, crystalline residue, which, after once crystallising from methyl alcohol, melted at 72°, had a_D $-22{\cdot}1°$, and consisted of l-*sylvestrene dihydrochloride*, and when this was decomposed by diethylaniline it yielded a specimen of l-*sylvestrene*, which distilled at 175—178° and had a_D $-66{\cdot}5°$.

The authors are greatly indebted to repeated grants from the Research Fund of the Royal Society, which largely covered the heavy expense involved in this investigation.

THE UNIVERSITIES OF ST. ANDREWS, OXFORD AND MANCHESTER.

CCXXXIII.—*Some Derivatives of Phorone. Part I.*

By Francis Francis and Francis George Willson.

The great ease with which nitrosotriacetonamine is catalytically decomposed into phorone, nitrogen, and water has been previously described (T., 1912, **101**, 2358), and the reaction has been utilised as a method for the determination of the concentration of hydroxyl ions (this vol., p. 1722).

There can be but little doubt that the formula used at present to represent the structure of phorone is correct, and that consequently this material affords an interesting basis for the study of chemical relations existing in a compound containing two adjacent pairs of conjugated double bonds—the so-called "cross-conjugated system." We desired to commence this study by the investigation of some simple derivative of phorone, in which the magnitude of the residual affinities should be altered.

As phorone tetrabromide was found to be readily converted into a dibromo-derivative, we determined to investigate this first, since its method of preparation pointed to the conclusion that it was a dibromophorone of the constitution

$$CMe_2:CBr\cdot CO\cdot CBr:CMe_2.$$

The replacement of two hydrogen atoms in phorone by bromine, however, results in the formation of a substance the properties of which differ more, from those of the parent material, than might have been expected.

The molecular refractivity of this dibromo-derivative showed an exaltation of 1·1, whereas phorone gives the abnormally high value of 3·0; further, the substance could not be directly brominated, did not combine with hydrogen bromide, and was curiously resistant towards oxidising agents.

The most characteristic reaction of this dibromo-derivative is the ease with which it is converted, by concentrated sulphuric acid, into a crystalline material of the molecular formula of a bromohydroxyphorone.

A study of the oxidation and reduction products of this derivative led us to formulate it as 1-*bromo*-2:2:3:3-*tetramethyl*bicyclo-[0, 1, 2]*pentan*-4-*ol*-5-*one*:

$$CO<\begin{matrix}CBr\text{---}CMe_2\\ |\qquad\quad |\\ C(OH)\cdot CMe_2\end{matrix},$$

although the peculiar action of bromine on it cannot be said

to receive a very satisfactory explanation from such a conception of its constitution.

When this *bicyclo*pentanone derivative is oxidised with alkaline permanganate it gives an excellent yield of a dibasic acid, $C_9H_{14}O_5$, and when this acid is warmed with concentrated sulphuric acid at 70—80° carbon monoxide is eliminated, and a quantitative yield of tetramethylsuccinic acid is obtained. The latter can also be obtained directly from the *bicyclo*pentanone by oxidation with chromic and sulphuric acids.

These changes may be represented as follows:

$$CO\!<\!\begin{array}{l}CBr\text{—}CMe_2\\ \;|\qquad\;\;|\\ C(OH)\cdot CMe_2\end{array} \longrightarrow \begin{array}{l}CO_2H\cdot CO\cdot CMe_2\\ \qquad\qquad\;\;|\\ \qquad CO_2H\cdot CMe_2\end{array} \longrightarrow CO + \begin{array}{l}CO_2H\cdot CMe_2\\ \qquad\quad\;\;|\\ CO_2H\cdot CMe_2\end{array}.$$

There can be little doubt that the oxidation of a derivative containing a five-membered ring had been carried out.

When the *bicyclo*pentanone derivative is reduced with zinc dust and glacial acetic acid, the yield of reduction product obtained is very unsatisfactory; but it becomes quantitative if the acetyl derivative is employed. The reduced acetyl derivative which is formed is a liquid possessing a terpene-like odour, readily saponified by alkali, and the free hydroxyl derivative is a crystalline material which so closely resembles the parent substance in all its properties that we assign to it a similar constitution, namely, 2:2:3:3-*tetramethyl*bicyclo[0, 1, 2]*pentan*-4-*ol*-5-*one*,

$$CO\!<\!\begin{array}{l}CH\text{——}CMe_2\\ \;|\qquad\quad\;|\\ C(OH)\cdot CMe_2\end{array}.$$

When the latter derivative, or the original *bicyclo*pentanone, is reduced in alkaline solution by sodium amalgam, a substance of the formula $C_9H_{16}O$ results. This forms a semicarbazone, condenses with difficulty with aldehydes, and in appearance, odour, taste, and volatility shows a striking resemblance to camphor.

There is but little doubt that it is 1:1:2:2-*tetramethyl*cyclo*pentan*-4-*one*,

$$CO\!<\!\begin{array}{l}CH_2\cdot CMe_2\\ \qquad\quad\;|\\ CH_2\cdot CMe_2\end{array},$$

and we consider that the difficulty experienced in obtaining condensation products with aldehydes may be ascribed to the accumulation of methyl groups in the molecule.

The action of bromine on the original *bicyclo*pentanone derivative results in the formation of a red, crystalline dibromo-derivative, $C_9H_{12}O_2Br_2$. It was found that 1-bromo-2:2:3:3-tetramethyl*bicyclo*[0, 1, 2]pentan-4-ol-5-one is not completely brominated in acetic acid solution unless one molecular proportion of

bromine was used for the purpose; this fact and the red colour of the derivative, suggesting an *o*-diketone structure, led us to formulate the bromination as follows:

$$\mathrm{CO}<\begin{array}{l}\mathrm{CBr{-}{-}CMe_2}\\ \mathrm{C(OH)\cdot CMe_2}\end{array} + \mathrm{Br_2} \rightarrow \mathrm{CO}<\begin{array}{l}\mathrm{CBr_2{-}{-}CMe_2}\\ \mathrm{CBr(OH)\cdot CMe_2}\end{array} \longrightarrow$$

$$\mathrm{HBr} + \mathrm{CO}<\begin{array}{l}\mathrm{CBr_2\cdot CMe_2}\\ \mathrm{CO{-}CMe_2}\end{array}$$

This explanation is based on K. Meyer's investigations of the action of bromine on substances of the nature of ethyl acetoacetate (*Annalen*, 1911, **380**, 212), and is supported by the fact that it was not found possible to brominate, in acetic acid solution, either the methyl or acetyl derivatives of 1-bromo-2:2:3:3-tetramethyl*bicyclo*[0, 1, 2]pentan-4-ol-5-one, clearly indicating that the hydrogen of the hydroxyl group played a part in the reaction.

The dibromo-derivative is characterised by the great ease with which it is reconverted into 1-bromo-2:2:3:3-tetramethyl*bicyclo*-[0, 1, 2]pentan-4-ol-5-one, and this decomposition on the basis of the constitution we have assigned to the former, namely, *5:5-dibromo-1:1:2:2-tetramethyl*cyclo*pentan-3:4-dione*, appears to indicate that under certain conditions it can functionate in the tautomeric form expressed by the formula

$$\mathrm{CO}<\begin{array}{l}\mathrm{CBr{-}{-}CMe_2}\\ \mathrm{C(OBr)\cdot CMe_2}\end{array}.$$

Although under one set of conditions one bromine atom is readily eliminated, yet such reagents as alkali hydroxides, or sodium acetate in alcoholic solution, yield bromine-free derivatives. The diacetate which results from the latter decomposition has been analysed, but the product from the action of alkalis is a syrup which, so far, we have been unable to investigate.

The only derivative of the red dibromo-derivative still containing two bromine atoms, which it has been found possible to isolate, is one resulting from the action of diazomethane on its ethereal solution. This is a colourless, crystalline material, differing only from the parent bromide by CH_2, and to which, based on our previous conceptions, we provisionally assign the constitution:

$$\mathrm{CH_2}<\begin{array}{l}\mathrm{O\cdot C{-}CBr_2}\\ \mathrm{O\cdot C\cdot CMe_2}\end{array}>\mathrm{CMe_2}.$$

The investigation is being continued, and it is hoped that further light will be thrown on these interesting substances.

Experimental.

Phorone tetrabromide has been described by Claisen, and is readily prepared by the action of bromine on phorone in carbon

disulphide or carbon tetrachloride solution. If the bromination is carried out in alcoholic solution an oil is obtained with properties altogether different from those of the tetrabromide, and it is proposed to investigate this substance at a later date.

Dibromophorone.

When the tetrabromide is dissolved in a little more than its own weight of cold pyridine, and the solution kept for twenty-four hours, the above is formed, and can be isolated by the addition of a large excess of water, when it is precipitated as an oil, which is obtained in quantitative yield and in a high state of purity by washing with water and then 30 per cent. sulphuric acid. The latter process must be thoroughly carried out, since the dibromo-derivative retains traces of pyridine with great tenacity, but when freed from this base the oil usually crystallises at once.

The compound crystallises in large, transparent, slightly yellow prisms, and melts at 32°. It may be distilled under greatly diminished pressure with but slight decomposition, it is extremely soluble in the usual organic solvents, possesses a faint odour resembling that of pine, and on exposure to the air rapidly becomes green:

0·4111 gave 0·5289 AgBr. Br = 54·7.

$C_9H_{12}OBr_2$ requires Br = 54·2 per cent.

The dibromo-derivative has a density of 1·552 at 37·4°, and the refractive index at this temperature for the *D*-line is 1·53941, and for the *C*-line 1·53460; this gives a molecular refractivity of 59·77 and 59·37 respectively, and an exaltation of 1·09 and 1·12, based on the formula we have assigned to this substance. The magnitude of this exaltation is what might have been expected in such a cross-conjugated system, but is very much less than that of phorone itself, which, according to Brühl, is 3·05.

The dibromo-derivative is either unacted on by reducing agents or else a very small yield of phorone is obtained. Oxidising agents have no action on it. When dissolved in carbon disulphide and treated with excess of bromine, it can be recovered unchanged; it is also unacted on when dissolved in a concentrated acetic acid solution of hydrogen bromide and allowed to remain for two weeks.

1-*Bromo*-2 : 2 : 3 : 3-*tetramethyl*bicyclo[0, 1, 2]*pentan*-4-*ol*-5-*one*.

The best method for the preparation of this substance consists in acting on dibromophorone in the cold with about three molecular proportions of concentrated sulphuric acid and allowing the mixture to remain for twenty-four hours. Bromine and hydrogen bromide

are evolved, and the product is isolated by pouring the solution on to crushed ice.

By using not more than 50 grams of the dibromo-derivative at one operation, a yield of 82 per cent. of the *bicyclo*pentanone derivative can be obtained.

The substance is best crystallised from dilute alcohol, from which solvent it separates in well-formed, colourless needles, melting at 116°. It is soluble in hot water, slightly volatile with steam, and its behaviour in this boiling solvent recalls that of benzoic acid. It is extremely stable towards concentrated sulphuric acid, and its solution in this medium may be heated to a temperature of 200° without showing any signs of decomposition:

0·1554 gave 0·2640 CO_2 and 0·0796 H_2O. C=46·33; H=5·69.
0·5768 „ 0·4636 AgBr. Br=34·14.
$C_9H_{13}O_2Br$ requires C=46·34; H=5·58; Br=34·34 per cent.

A determination of the molecular weight by the ebullioscopic method, using acetone as solvent, gave the following result:

1·0221 in 19·8 gave Δt 0·360. M.W.=244.
$C_9H_{13}O_2Br$ requires M.W.=233.

This compound possesses well-marked acidic properties, a hot aqueous solution reddens litmus paper, it is easily soluble in solutions of the alkalis and in alkaline carbonates, and the sodium salt separates from concentrated solutions in characteristic silky needles.

We were unable to obtain either an oxime or semicarbazide, probably due to the presence of substituents on either side of the carbonyl group.

The presence of one hydroxyl group was confirmed by the formation of the following derivatives:

The *acetyl* derivative, prepared by boiling the *bicyclo*pentanone for one hour with excess of acetic anhydride, recrystallises from dilute acetic acid in long, colourless needles, melting at 74°:

0·1562 gave 0·2782 CO_2 and 0·0807 H_2O. C=48·57; H=5·74.
0·605 „ 0·4172 AgBr. Br=29·34.
$C_{11}H_{15}O_3Br$ requires C=48·01; H=5·45; Br=29·09 per cent.

The *benzoyl* derivative was obtained in the usual way, using pyridine as solvent. After crystallisation from dilute alcohol it melts at 92°:

0·184 gave 0·3825 CO_2 and 0·0892 H_2O. C=56·7; H=5·38.
$C_{19}H_{17}O_3Br$ requires C=56·98; H=5·04 per cent.

The *carbomethoxy*-derivative, after crystallisation from dilute alcohol and ether, melts at 75—77°:

0·205 gave 0·3396 CO_2 and 0·0954 H_2O. C=45·18; H=5·17.
$C_{11}H_{15}O_4Br$ requires C=45·36; H=5·15 per cent.

Oxidation of 1-*Bromo*-2:2:3:3-*tetramethyl*bicyclo[0, 1, 2]*pentan*-4-*ol*-5-*one*.

Ten grams of this derivative were dissolved in an excess of potassium hydroxide and oxidised with a solution of 15 grams of potassium permanganate, care being taken not to allow the temperature to rise. On acidification and repeated extraction with ether, 8 grams of an oil were obtained, which set to a very hard, crystalline mass on keeping. After solidification it could be recrystallised from toluene, and melted at 139°:

0·2116 gave 0·4732 CO_2 and 0·1492 H_2O. C=53·42; H=6·86.
$C_9H_{14}O_5$ requires C=53·46; H=6·93 per cent.

A determination of the molecular weight by the ebullioscopic method, using acetone as solvent, gave the following result:

0·1612 in 12·70 gave Δt 0·120°. M.W.=180.
$C_9H_{14}O_5$ requires M.W.=202.

This substance was readily soluble in water, gave a strongly acid solution, and was shown to be dibasic by an analysis of its *silver salt*:

0·4110 gave 0·2325 Ag. Ag=52·60.
$C_9H_{12}O_5Ag_2$ requires Ag=51·93 per cent.

In order to determine the number of hydroxyl groups, a specimen of the pure acid was treated with excess of diazomethane in ethereal solution. The resulting oil was fractionated in a vacuum, and the main bulk of the methyl derivative boiled at 160°/50 mm. On keeping for a long period this oil set to a crystalline mass, which melted at 93—97° on recrystallisation from benzene and light petroleum. The analysis showed that a dimethyl derivative only had been formed, and hence that there were only two hydroxyl groups present:

0·2133 gave 0·1436 CO_2 and 0·1479 H_2O. C=56·71; H=7·71.
$C_{11}H_{18}O_5$ requires C=57·39; H=7·82 per cent.

Since this acid can be quantitatively converted into dimethylsuccinic acid, there can be no doubt that it is *a-keto-βγ-tetramethylglutaric acid*, $CO_2H·CO·CMe_2·CMe_2·CO_2H$.

On reduction with sodium amalgam in alkaline solution this acid passes quantitatively into the *lactone* of *a-hydroxy-βγ-tetramethylglutaric acid*, an oil which slowly solidifies to a crystalline mass; this may then be purified by recrystallisation from benzene and light petroleum, and melts at 68°:

0·2168 gave 0·4578 CO_2 and 0·1503 H_2O. C=57·58; H=7·65.
$C_9H_{14}O_4$ requires C=58·06; H=7·52.

An analysis of the *silver* salt of this lactonic acid showed that it was monobasic:

0·4880 gave 0·1798 Ag. Ag=36·85.
$C_9H_{13}O_4Ag$ requires Ag=36·85 per cent.

When α-keto-$\beta\gamma$-tetramethylglutaric acid was warmed to 80° with concentrated sulphuric acid, carbon monoxide was evolved, and a quantitative yield of tetramethylsuccinic acid obtained. This acid (m. p. 180—190°) gave correct data on analysis, and was characterised by conversion into its anhydride, which melted at 147°, and also gave correct analytical data.

Tetramethylsuccinic acid was also obtained by the direct oxidation of the *bicyclo*pentanone derivative with chromic acid.

*Reduction of 1-Bromo-2:2:3:3-tetramethyl*bicyclo[0, 1, 2]*pentan-4-ol-5-one.*

This derivative gives only a very poor yield of reduction product when treated with zinc dust and glacial acetic acid, but when the acetyl derivative is used an excellent yield of the acetyl derivative of 2:2:3:3-*tetramethyl*bicyclo[0, 1, 2]*pentan-4-ol-5-one* is obtained. This derivative is an oil, which is easily saponified by warming with dilute alkalis; when this solution is acidified and extracted with ether, the parent substance is obtained, which fuses at 86° on recrystallisation from boiling water.

In appearance and solubility it closely resembles the bromo-derivative; it also possesses a very similar, but somewhat more pungent, odour, and shows the same acid properties:

0·2190 gave 0·5618 CO_2 and 0·1788 H_2O. C=69·96; H=9·07.
$C_9H_{14}O_2$ requires C=70·13; H=9·09 per cent.

The *benzoyl* derivative, prepared by the ordinary method, melts at 69° on crystallisation from dilute alcohol:

0·2324 gave 0·6330 CO_2 and 0·1470 H_2O. C=74·29; H=7·03.
$C_{16}H_{18}O_3$ requires C=74·42; H=6·98 per cent.

When 1-bromo-2:2:3:3-tetramethyl*bicyclo*[0,1,2]pentan-4-ol-5-one is reduced in alkaline solution by 2 per cent. sodium amalgam, a strong odour of camphor soon becomes apparent, and the reduction product separates in flakes which can be extracted with ether.

The derivative is purified with difficulty by crystallisation from dilute alcohol and ether; it melts at 130°, and sublimes so readily that it cannot be dried in a vacuum. The same substance can also

be obtained by the reduction, under similar conditions, of 2:2:3:3-tetramethyl*bicyclo*[0, 1, 2]pentan-4-ol-5-one.

The material is only sparingly soluble in water, but dissolves in the ordinary organic solvents, and has an appearance, odour, and taste curiously similar to that of camphor, and, like that substance, feels the same when pressed or cut with a spatula:

0·2086 gave 0·5884 CO_2 and 0·2152 H_2O. C=76·91; H=11·47.
$C_9H_{16}O$ requires C=77·14; H=11·43 per cent.

A determination of the molecular weight by the ebullioscopic method, using acetone as solvent, gave the following result:

1·4367 in 16·36 gave Δt 1·008. M.W.=148.
$C_9H_{16}O$ requires M.W.=140.

The *semicarbazone* obtained in the usual manner melted at 223° on recrystallisation from dilute alcohol:

0·144 gave 26·6 c.c. N_2 at 13·5° and 759·7. N=21·78.
$C_{10}H_{19}ON_3$ requires N=21·32 per cent.

There can be but little doubt that the substance described is 1:1:2:2-*tetramethyl*cyclo*pentan*-4-*one*, but, unlike cyclic ketones of this class, it does not condense at all readily with aldehydes. Both with benzaldehyde and with *o*- and *m*-nitrobenzaldehyde, under the influence of sodium ethoxide, small quantities of yellow condensation products were obtained, but analysis showed that these were mixtures of mono- and di-benzylidene derivatives, which, with the small amount at our command, we were unable to separate.

When 1:1:2:2-tetramethyl*cyclo*pentan-4-one is oxidised with hydrogen peroxide in alkaline solution an acid results, which may be crystallised from a small quantity of water, or from benzene, and melts at 131°. The analysis indicated that this substance was *αβ-tetramethylglutaric acid*, $CO_2H{\cdot}CH_2{\cdot}CMe_2{\cdot}CMe_2{\cdot}CO_2H$:

0·2272 gave 0·4794 CO_2 and 0·1662 H_2O. C=57·53; H=8·14.
$C_9H_{16}O_4$ requires C=57·45; H=8·51 per cent.

Action of Bromine on 1-*Bromo*-2:2:3:3-*tetramethyl*-bicyclo[0, 1, 2]*pentan*-4-*ol*-5-*one*.

Bromine does not act on the above compound in carbon disulphide solution, but one molecular proportion gives a quantitative yield of a dibromo-derivative when the operation is carried out in glacial acetic acid. The compound is insoluble in water, and may be purified by rapid crystallisation from alcohol. It is an orange, crystalline substance, melting at 182°.

From the analysis and molecular-weight determination we consider that this substance is 5:5-*dibromo*-1:1:2:2-*tetramethyl*cyclo-*pentane*-3:4-*dione*:

0·1457 gave 0·185 CO_2 and 0·0507 H_2O. C=34·63; H=3·87.
0·4587 ,, 0·5602 AgBr. Br=51·96.
$C_9H_{12}O_2Br_2$ requires C=34·61; H=3·85; Br=51·28 per cent.

The molecular weight was determined by the ebullioscopic method, using acetone as solvent:

0·3466 in 14·79 gave Δt 0·178. M.W.=288.
$C_9H_{12}O_2Br_2$ requires M.W.=312.

Neither the acetyl nor the methyl derivatives of 1-bromo-2 : 2 : 3 : 3-tetramethyl*bicyclo*[0, 1, 2]pentan-4-ol-5-one could be brominated in acetic acid solution.

By far the most characteristic reaction of this dibromo-derivative was the case with which it was reconverted into the substance from which it was obtained; a decomposition brought about quantitatively by concentrated sulphuric acid or by reduction with zinc dust and glacial acetic acid, and partly by boiling with water, alcohol, or acetone.

This decomposition clearly points to the fact that one bromine atom is situated differently from the other.

Although under the above conditions one bromine atom alone is eliminated, yet when the dibromo-derivative is acted on by alkalis in aqueous suspension a substance is obtained free from bromine. The yield of the latter, however, is small, and the substance is a syrup, which we have been unable to obtain in quantity in the crystalline form. A small specimen recrystallised from benzene in light petroleum melted at 68°.

When the dibromo-derivative is boiled with an excess of alcoholic sodium acetate a crystalline *diacetate* is obtained, which melts at 100—102° on recrystallisation from dilute acetic acid:

0·1468 gave 0·3118 CO_2 and 0·0898 H_2O. C=57·91; H=6·79.
$C_{13}H_{18}O_6$ requires C=57·77; H=6·66 per cent.

This diacetate is readily decomposed by dilute alkalis, and the resulting substance is a syrup which we believe to be identical with that mentioned in the last paragraph. A small quantity of this was also obtained in the crystalline form and melted at 67°, and this melting point remained unchanged when the substance was mixed with some of the product obtained by the action of alkalis on the dibromo-derivative.

The only derivative of the latter compound that we have been able to obtain, which still contains two bromine atoms, is that which results when its ethereal solution is treated with diazomethane. This derivative, which is colourless, crystallises indifferently, and the crystals feel sticky, although showing a definite melting point of 190° after repeated recrystallisations from dilute acetic acid:

0·2274 gave 0·3066 CO_2 and 0·0904 H_2O. C = 36·77; H = 4·42.
0·4578 „ 0·5299 AgBr. Br = 49·25.
$C_{10}H_{12}O_2Br_2$ requires C = 36·81; H = 4·29; Br = 49·08 per cent.

Our thanks are due to Mr. D. A. Clibbens for the great assistance he gave one of us in the preliminary investigation of the *cyclo*pentanone and its dibromo-derivative.

THE CHEMICAL DEPARTMENT,
UNIVERSITY OF BRISTOL.

CCXXIV.—*Amalgams Containing Silver and Tin.*

By WILLIAM ARTHUR KNIGHT and REGINALD ARTHUR JOYNER.

THE present investigation is a continuation of work done in this laboratory by one of us on the chemistry of the ternary system tin-silver-mercury (T., 1911, **99**, 195; also McBain and Joyner, *Dental Cosmos*, June, 1912). In that communication it was firmly established that freshly filed alloys of silver and tin require about twice as much mercury for amalgamation as filings which have been heated to 100° for half-an-hour, or which have been kept at room temperature for several months after filing. The latter kinds of filings are said to be "aged." In addition to a thorough investigation of this "ageing" of filings of silver–tin alloys, the communication mentioned above contained an account of work done on the chemistry of the binary systems silver–tin, silver–mercury, tin–mercury, whilst the ternary system silver–tin–mercury was studied at temperatures up to 63°.

The object of the present investigation was to check and confirm some of the previous conclusions with regard to ageing, and to study the ternary diagram at higher temperatures.

Throughout the present communication the composition of the alloys and amalgams is everywhere expressed in atomic percentages, but the percentages of tin and silver in the liquid amalgams as given in tables III—VI of the previous communication are percentages by weight.

PART I.

The Ageing of Filings of Alloys of Silver and Tin.

Although no satisfactory explanation of the mechanism of this process has been advanced, its existence was proved conclusively

by the results given in the previous communication. It has been suggested (H. B. Baker, *Ann. Reports*, 1911, **8**, 36) that the experiments described did not absolutely disprove the hypothesis that the ageing of a dental alloy may be due to a superficial film of oxide formed during the heating, especially since many metals oxidise very readily when they are ground in an agate mortar.

We desire to take this opportunity (compare Baker, *loc. cit.*, with Joyner, *loc. cit.*, p. 195) of stating categorically that it is an obvious *sine qua non* of work such as that described in this and the previous communication that all experiments on alloys, filings, or amalgams above room temperature are carried out in a reducing atmosphere of hydrogen or coal gas. This also applies to the preparation of the alloys when fusing their constituents together. Apart from the few particular experiments specially indicated, this condition has been observed throughout.

The following further experiments were therefore carried out by one of us, and fully confirm those previously published by the other:

(1) A quantity of the alloy Ag_3Sn was very slowly filed, the bar of alloy being cooled in running water every ten seconds. Some of this filed alloy was pulverised in an agate mortar, and was then weighed and shaken for two minutes with excess of mercury. The excess of mercury was squeezed out through chamois leather by the application of a 56 lb. weight (25 kilos.), as described in the previous communication (*loc. cit.*, p. 198). The amalgam remaining was then weighed. It was found that

$$\frac{\text{Wt. of mercury retained}}{\text{Wt. of alloy taken}} = \frac{6{\cdot}081}{2{\cdot}414}, = \frac{2{\cdot}52}{1}.$$

These filings have therefore remained "unaged" in spite of having been ground fine in an agate mortar. This confirms the experiment previously published (Joyner, *loc. cit.*, p. 203), which Baker appears to have overlooked.

(2) A similar experiment was performed, but the filings of the alloy Ag_3Sn were "aged" before pulverisation by heating for half-an-hour at 100° in an atmosphere of coal-gas. It was found that

$$\frac{\text{Wt. of mercury retained}}{\text{Wt. of alloy taken}} = \frac{3{\cdot}448}{3{\cdot}212}, = \frac{1{\cdot}07}{1}.$$

These filings are therefore still "aged." Hence pulverisation in an agate mortar does not age unaged alloy, nor does it unage aged alloy. This shows that the hypothesis that ageing may be due to

superficial oxidation is untenable. For, if such were the case, pulverisation would either remove the film of oxide exposing fresh surfaces of alloy on which mercury would readily react, thus unageing those filings, or, likewise contrary to fact, unaged filings would thereby become aged.

(3) Two lots of filings of the alloy Ag_3Sn were prepared similarly, and were heated in sealed tubes for half-an-hour at 100°. The tubes had been washed out four times with coal gas after introducing the filings, and finally one tube was filled with coal gas whilst the other was thoroughly exhausted by a Fleuss pump before they were sealed up After heating, the contents of each tube were pulverised in the agate mortar, amalgamated, and the excess of mercury squeezed out as before. The results obtained were as follows:

(a) Tube Filled with Coal Gas.

$$\frac{\text{Wt. of mercury retained}}{\text{Wt. of alloy taken}} = \frac{1{\cdot}522}{1{\cdot}806}, = \frac{0{\cdot}84}{1}.$$

(b) Tube Exhausted.

$$\frac{\text{Wt. of mercury retained}}{\text{Wt. of alloy taken}} = \frac{1{\cdot}877}{2{\cdot}400}, = \frac{0{\cdot}78}{1}.$$

Hence both lots of filings were still aged.

(4) Efforts were again made to "age" a solid bar of alloy. The bar of Ag_3Sn was heated in a sealed tube filled with coal gas for five days at 115°. After filing, pulverising, and amalgamating as before, it was found that

$$\frac{\text{Wt. of mercury retained}}{\text{Wt. of alloy taken}} = \frac{5{\cdot}112}{2{\cdot}068}, = \frac{2{\cdot}47}{1}.$$

On heating to 115° for a further four days, filings from the same bar gave

$$\frac{\text{Wt. of mercury retained}}{\text{Wt. of alloy taken}} = \frac{2{\cdot}33}{1},$$

whilst after six days more at the same temperature

$$\frac{\text{Wt. of mercury retained}}{\text{Wt. of alloy taken}} = \frac{2{\cdot}29}{1}.$$

The bar has therefore remained "unaged." It seems, therefore, no longer possible to ascribe ageing to any (uncatalysed) polymorphic change, since ageing does not take place in a bar of alloy

heated during several weeks, whereas it occurs with unfailing regularity in filings heated for half-an-hour.

(5) Ageing might be due to sorption of oxygen by the filings, but such oxygen cannot have any effect if magnesium is added to the alloy before filing. Hence, in order to test this hypothesis, the following experiment was carried out.

Part of a bar of the alloy Ag_3Sn was melted with about 1 per cent. of its weight of magnesium in an atmosphere of coal gas. After allowing the resulting alloy to solidify, it was re-melted with vigorous shaking, and again allowed to solidify. The alloy prepared in this way must have been thoroughly mixed. Filings of this alloy were amalgamated, and the excess of mercury squeezed out exactly as in previous experiments. The result gave:

$$\frac{\text{Wt. of mercury retained}}{\text{Wt. of alloy taken}} = \frac{4{\cdot}733}{2{\cdot}143},$$
$$= \frac{2{\cdot}21}{1}.$$

A second quantity of these filings was "aged" before amalgamation, and it was found that

$$\frac{\text{Wt. of mercury retained}}{\text{Wt. of alloy taken}} = \frac{2{\cdot}977}{2{\cdot}781},$$
$$= \frac{1{\cdot}07}{1}.$$

This experiment thus disproves the hypothesis that ageing is due to sorption of oxygen by the filings.

Although the mechanism of ageing is as yet quite unknown to us, it might be due to a polymorphic change, which, as it does not take place with sensible velocity until the bar of alloy is filed up, may possibly be enormously accelerated by the iron or products of iron introduced during the filing.*

Part II.

The Ternary System: Silver–Tin–Mercury.

In the previous communication it is stated that there are two groups of equilibria in this system corresponding with higher and lower temperatures respectively. Further investigation, however, has shown that, although this view is not quite strictly correct, it is true for all practical purposes. The evidence in favour of it was that the cooling curves of all amalgams of silver and tin show breaks at temperatures between 65° and 100°. This might have

* That a change does take place in the Ag_3Sn filings we have established by density determinations; these will be included in a later communication.

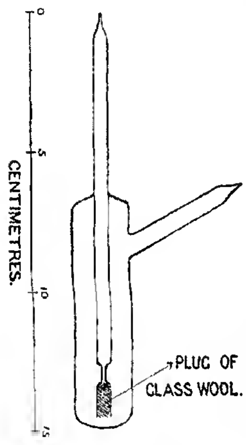
been interpreted as being due to the formation of a ternary compound at higher temperatures. These breaks may also be taken as indicating that the particular amalgam under consideration has crossed from a field of three phases (*E* in Fig. 1) to a field of two phases (*B* in Fig. 1), owing to the broadening out of this latter region as the temperature rises. It is shown in the sequel that the latter interpretation is correct, and that no ternary compound is formed.

Systems Containing Wholly or Partly Liquid Amalgams.

The study of the composition of the liquid amalgams in contact with one or more solids not only establishes by direct experiment the exact delimitations of the liquids which are so important a feature of this system, but derives special significance when interpreted in the light of the phase rule. This mode of attack, which is not usually available, enables us to deduce with certainty, from the position and shape of the liquid region, the nature and the composition of the solids capable of existing in contact with these liquids. The phase rule predicts that, in a ternary system such as the present, not more than two solids can simultaneously exist in contact with liquid at any given temperature. Where two solids are present the liquid will have a fixed composition lying at the intersection of two of the curves bounding the liquid field. Liquids situated along the smooth boundary curves themselves can be in contact with only one solid element or compound or solid solution; thus the number of solid phases present is known. Finally, the nature and composition of the solids present can be deduced from a knowledge of the initial percentage composition of the system and the composition of the resulting liquid.

This method has here been employed at the following temperatures: 63°, 90°, 166°, and 214°. Thus for each temperature we have obtained an equilibrium diagram showing the composition and extent of all saturated and unsaturated liquids (region denoted by the letter *A* in the diagrams), together with the delimitation of all the adjacent heterogeneous fields, leaving only a small portion of the diagram consisting of solids very rich in silver, but containing very little tin still to be investigated. For this the ordinary metallographic methods will be available. The result is to disprove the existence of any ternary compound of silver, tin, and mercury, but, on the other hand, to demonstrate the existence of a single series of solid solutions indistinguishable from "*Arbor Dianae,*" Ag_3Hg_4, at room temperature. At high temperatures this series of solid solutions lengthens out from this composition of Ag_3Hg_4 roughly in the direction of Ag_3Sn as the temperature is raised.

In order to determine the composition of the liquid phase at any temperature, weighed amounts of the three metals were introduced into the reaction tube, from which all air was removed by washing out the tube by means of coal gas after introducing the metals. The reaction tubes at the lower temperatures, where the vapour pressure of mercury is small, were not completely immersed in the thermostat. At the higher temperatures the tubes were sealed off and totally immersed, the drawn out portion being scratched so as to admit of breaking it within a rubber tube connected with hydrogen or coal gas while keeping it still in the thermostat. These tubes for the higher temperatures were of the shape and approximately of the size shown. Scrupulous care must be taken to ensure that all the solid has really come into contact with all the liquid.



REACTION TUBE.

At 166° a heavy oil was employed as thermostat liquid. The particular oil used was obtained through Messrs. Baird and Tatlock from Price's Patent Candle Co., and gave off little odour even at 166°. At 214° the oil was replaced by the eutectic mixture of potassium and sodium nitrates (45·5 per cent. by weight of the latter), to which a quantity of lithium nitrate had been added sufficient to ensure its remaining liquid at about 205°, as the eutectic mixture of potassium and sodium nitrates solidifies at 218°. No difficulty was experienced in maintaining the temperature of the melted nitrates constant to within 0·2° during any individual experiment, although the mercury regulator was simply a length of iron gas piping.

After the reaction tubes had remained in the thermostat for a sufficiently long time to ensure the attainment of equilibrium—this time varied from four days at the low temperatures to as many hours at the high temperatures—part of the liquid phase was removed and analysed in the same way as is described in the previous communication.

The tables which follow give:

(1) The gross composition of the mixtures with which the reaction tubes were charged.

(2) The composition of the liquid phase as determined by analysis.

(3) The letters by which the corresponding points on the diagram are designated.

The positions of the points representing the gross compositions are indicated thus ⊙, whilst the points on the liquid curves are shown thus ×, corresponding points being represented everywhere by the same letter. All compositions are given in atomic percentages of the metals employed.

TABLE I.

Temp. 63·10°±0·05.

Gross composition.			Composition of liquid phase.			Point on diagram.
Ag.	Sn.	Hg.	Ag.	Sn.	Hg.	
35·0	2·0	63·0	0·21	1·82	98·0	*a*
35·0	2·75	62·25	0·36	4·04	95·6	*b*
35·0	3·5	61·5	0·06	4·16	95·77	*c*

The atomic percentage of silver in the liquid phase corresponding with the point *c* is too low owing to error in the analysis, but previous determinations (T., 1911, **99**, 208) in the case of saturated amalgams render this of little importance.

From the results of table I combined with those given on p. 208 of the previous communication, it is possible to construct the cross-section of the thermal diagram at this temperature; thus when the results mentioned last are re-calculated in atomic percentages, we have the following values:

Solubility of silver in mercury at 63° – 0·191 at. per cent.

Solubility of tin in mercury at 63° = 3·884 at. per cent.

The other results of this table represent amalgams saturated with respect to both silver and tin, and their liquid phases coincide with the intersection of the liquid curves at *c*.

The cross-section at 63° of the thermal diagram is given in Fig. 1.

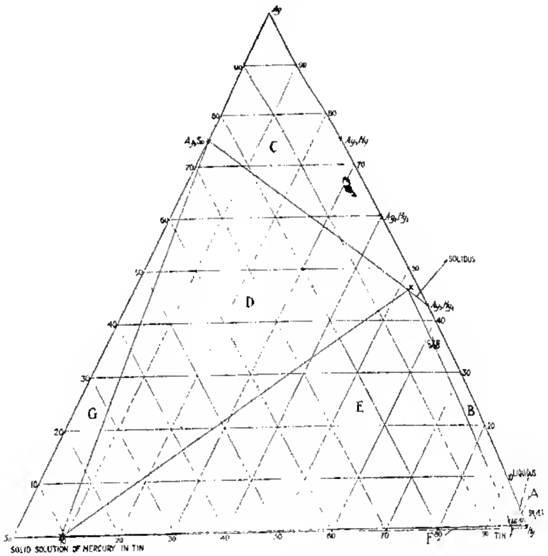
The explanation of this figure is as follows: The pure metals occupy the angular points of the equilateral triangle. On the side Ag–Sn is marked the position of the only compound which silver forms with tin, namely, Ag_3Sn, containing 75 atoms per cent. of silver. Now silver and mercury form three compounds, Ag_3Hg_4, Ag_3Hg_2, and Ag_3Hg, which are shown in their proper positions on the side Ag–Hg. Tin and mercury do not form a compound, but the solid crystallising out at any temperature consists of a solid solution of mercury in tin. At 63° this solid solution contains 9·5 atoms per cent. of mercury (K. Bornemann, "Die binären Metallegierungen," Teil II., Tafel 14). This point is marked on the

Sn–Hg side of the triangle. In addition there is shown the position of the saturated solution of silver in mercury at "Silver," and that of the saturated solution of tin in mercury at "Tin." On joining up the points as shown in the figure, it will be seen that at 63°:

(1) All points in the field *A* represent liquids. This field *A* is bounded by two continuous curves and by the Sn–Hg side of the triangle.

(2) All mixtures the compositions of which are represented by

Fig. 1.



points in the field *B* give a liquid represented by a point on the liquidus, together with a solid solution represented by a corresponding point on the solidus. It is a geometrical requirement that if a straight line is drawn from the point on the liquidus to the point representing the gross composition of the original mixture this straight line must pass through the point on the solidus representing the composition of the solid solution. That the solids in this heterogeneous field must be solid solutions is a requirement of the phase rule. For by the phase rule it follows that in a system consisting of three metals there can only be one solid phase

in regions where the liquid phase varies, and a series of solid solutions is the only way in which this single phase can be constituted, since the locus of the prolongations is a curve. Had the solid been a definite compound, all the prolongations would have passed through the one point representing its composition on the diagram. That there is good reason for considering the line drawn from Ag_3Hg_4 to X as approximately the solidus will be seen later.

(3) In all regions such as *G* a mixture of the three metals in the proportions represented by any point within the area considered gives the substances represented by the angular points of that region; thus any point within the area *G* gives the three substances Ag_3Sn, Sn, and saturated solution of mercury in tin. The proportions in which these substances are formed depends on the position of the point representing the gross composition of the original mixture.

The results of table I can be exhibited in a different way as follows: We can calculate for each point the number of atoms of silver and of tin associated with 100 atoms of mercury. The results of this calculation are as follows:

TABLE I*a*.

Point on diagram.	No. of atoms of silver to 100 atoms of mercury.	No. of atoms of tin to 100 atoms of mercury.
"Silver"	0·19	—
a	0·21	1·86
b	0·38	4·23
c	(as *b* 0·38)	4·34
"Tin"	—	4·04

The number of atoms of silver thus obtained may be plotted as ordinates against the number of atoms of tin as abscissæ. Taken in conjunction with similar diagrams at higher temperatures (see below) consisting of two flat curves meeting at a point, it is clear that no definite compound between silver, tin, and mercury is formed.

TABLE II.

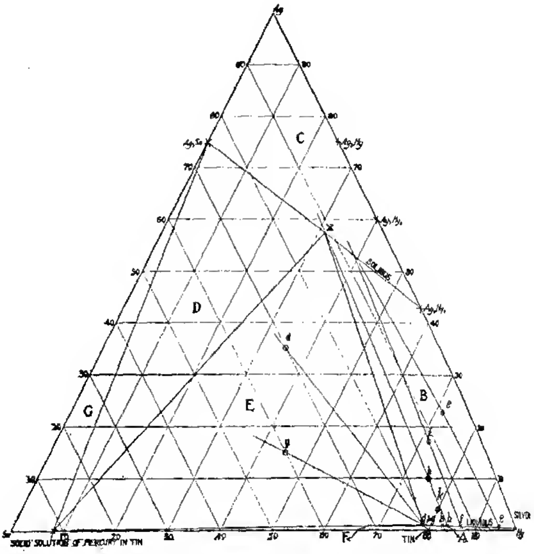
Temp. 90·0°±0·2.

Gross composition.			Composition of liquid phase.			Point on diagram.
Ag.	Sn.	Hg.	Ag.	Sn.	Hg.	
	Pure silver		0·38	—	99·67	"Silver"
35·0	30·0	35·0	1·00	20·6	78·4	*d*
22·8	5·7	71·5	0·53	4·2	95·3	*e*
17·1	11·4	71·5	0·80	12·9	86·3	*f*
15·0	40·0	45·0	0·96	20·5	78·5	*g*
10·0	15·0	75·0	0·88	15·7	83·4	*h*
4·0	16·0	80·0	0·92	16·6	82·4	*k*
	Pure tin		—	20·0	80·0	"Tin."

The last value is taken from the diagram in Bornemann's book previously referred to.

The results of table II are shown in Fig 2, where the different fields are represented by the same letters as in Fig. 1. We see that the liquid field A has increased considerably in length, and also that it is broader than was the case at 63°. All mixtures the gross compositions of which are represented by points falling within the area A are completely liquid at 90°. The heterogeneous field B has also increased in size. All mixtures represented

Fig. 2.



initially by points within the area B give a liquid the composition of which is represented by a point on the liquidus, together with a solid solution represented by the corresponding point on the solidus. Mixtures represented by points within the triangle E always give saturated solutions of tin and silver in mercury; thus the liquids given by the mixtures the compositions of which are d and g are identical, and their composition is represented by the intersection of the boundary curves of the field A. It will be evident from the above that mixtures represented by points falling within any of the other areas give the substances represented by

he angular points of the triangle in which the points fall. It is probable that the cross-section of the solidus is not a straight line as shown in the figure, but as yet the actual shape of the solidus is not known as accurately as is the case with the liquidus. This point will be referred to again.

In the same way that we obtained the results of table I*a* from table I, we can get those of table II*a* from table II.

TABLE II*a*.

Point on Diagram.	No. of atoms of silver to 100 atoms of mercury.	No. of atoms of tin to 100 atoms of mercury.
"Silver"	0·33	—
d	1·28	26·3
e	0·56	4·4
f	0·93	14·9
g	1·22	26·1
h	1·06	18·8
k	1·12	20·0
"Tin"	—	25·0

Special attention was devoted to the diagram at 166·5°, the results being as follows:

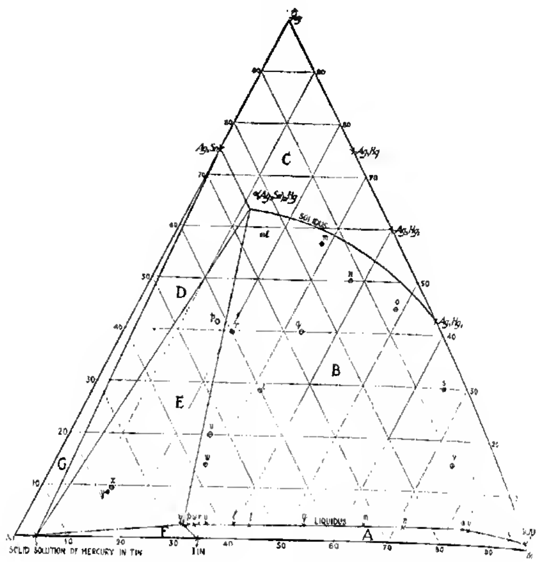
TABLE III.

Temp. 166·5°±0·5.

Gross composition.			Composition of liquid phase.			
Ag.	Sn.	Hg.	Ag.	Sn.	Hg.	Point on diagram.
	Pure silver		1·13	—	98·87	"Silver"
58·3	25·0	16·7	3·11	57·6	39·3	*l*
57·1	14·3	28·6	3·57	32·7	63·7	*m*
50·0	12·5	37·5	2·73	25·6	71·7	*n*
44·8	6·6	48·6	3·20	13·9	82·9	*o*
41·7	41·7	16·6	2·80	66·2	31·0	*p*
40·0	26·7	33·3	3·02	44·3	52·7	*q*
39·9	39·9	20·2	2·82	64·1	33·1	*r*
29·9	4·9	65·2	1·41	4·6	94·0	*s*
28·8	40·0	31·2	2·70	54·4	42·9	*t*
20·0	53·5	26·5	2·95	62·5	34·5	*u*
15·1	10·1	74·8	2·80	13·0	84·2	*v*
14·3	57·1	28·6	2·60	65·0	32·4	*w*
9·6	77·1	13·3	1·60	66·6	31·8	*x*
8·7	78·3	13·0	2·73	67·1	30·2	*y*
	Pure tin		—	65·6	34·4	"Tin"

The cross-section of the thermal diagram at 166·5° is given in Fig. 3.

FIG. 3.



The results of table III can be arranged in the following way:

TABLE III*a*.

Point on diagram.	No. of atoms of silver to 100 atoms of mercury.	No. of atoms of tin to 100 atoms of mercury.
"Silver"	1·14	—
l	7·91	146·6
m	5·60	51·3
n	3·81	35·7
o	3·86	16·8
p	9·03	213·6
q	5·73	84·1
r	8·52	193·7
s	1·50	4·9
t	6·29	126·8
u	8·55	181·2
v	3·33	15·4
w	8·02	200·6
x	5·03	209·4
y	9·04	222·2
"Tin"	—	190·8

On plotting these points we again obtain two smooth curves meeting at a point.

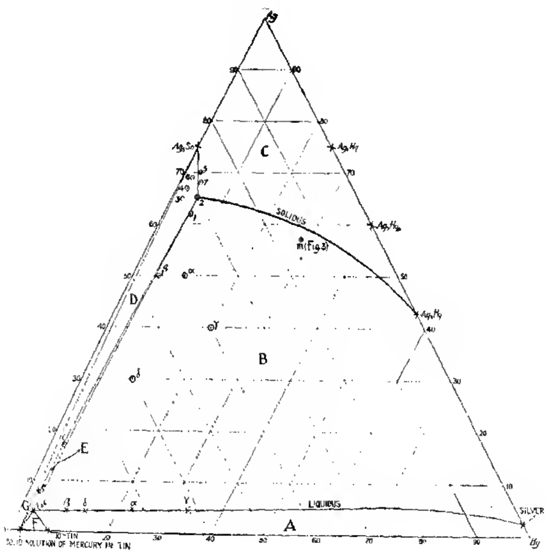
TABLE IV.

Temp. 214·0°±0·5.

Gross composition.			Composition of liquid phase.			Point on diagram.
Ag.	Sn.	Hg.	Ag.	Sn.	Hg.	
	Pure silver		2·3	—	97·7	"Silver."
50·0	40·0	10·0	4·8	72·7	22·5	α
50·0	45·0	5·0	4·3	86·0	9·7	β
40·0	40·0	20·0	5·1	61·4	33·5	γ
30·0	60·0	10·0	4·0	82·3	13·7	δ
17·3	80·3	2·4	3·9	93·2	2·9	ε
8·0	90·0	2·0	3·8	93·2	3·0	ζ
	Pure tin		—	92·0	8·0	"Tin."

The cross-section of the thermal diagram at 214° is given in Fig. 4. It is similar to those obtained at lower temperatures, and the remarks made there apply here also.

FIG. 4.



The Solidus.

The position and shape of the solidus has not been determined as accurately as the liquidus. The method by which its approxi-

mate position has been found is as follows: From measurements of the vapour pressures of silver amalgams, which are being carried out by one of us, it is known that Ag_3Hg_4 is solid and stable at 300°, since it has at that temperature a vapour pressure considerably lower than that of mercury. From this it appears that a mixture of mercury and silver gives rise to Ag_3Hg_4 and a saturated solution of silver in mercury. Hence the solidus passes through the point Ag_3Hg_4, the corresponding point on the liquidus at any temperature giving the concentration of the solution of silver in mercury at that temperature. During the present series of measurements it was found that the mixture *m* (Fig. 3) gave rise to a small amount of liquid phase. Therefore the solidus lies slightly above *m*. A mixture corresponding with $(Ag_3Sn)_2Hg$ gave absolutely no indication of a liquid phase at 166°. Hence the solidus at 166° passes through Ag_3Hg_4, slightly above *m*, and somewhat below $(Ag_3Sn)_2Hg$. In the same way at 214° its position is the same thus far, but the left hand end was investigated in the following way: Mixtures corresponding with the compositions given by the points 1, 2, 3 . . . 7 were made up, and were heated to 214° for several hours. These mixtures were then examined carefully for the presence or absence of liquid. The compositions of these points are as follows:

	Ag.	Sn.	Hg (at.%)	Presence or absence of liquid.
(1)...............	62	33	5	Plenty of liquid.
(2)...............	65	30	5	If present, amount of liquid was extremely small.
(3)	65	33	2	Certainly gave liquid.
(4)...............	67	31	2	Certainly gave liquid.
(5)...............	70	27	3	Gave no liquid.
(6)...............	69	29	2	Very small amount of liquid.
(7)...............	68	28	4	Gave no liquid.

In the case of (5), (6), and (7) the mixtures were heated at 250° for twelve hours before being introduced into the thermostat at 214°, thus ensuring that equilibrium was attained.

It is evident that, if the *whole* of the liquid phase could be withdrawn in each determination, the position of the corresponding point on the solidus could be readily found with considerable accuracy. For if we had $(m+n)$ grams of the mixture A in the reaction tube, and if this gave rise to m grams of liquid B, then the corresponding point C on the solidus could be found by producing BA to C, so that $n \times CA = m \times BA$. Unfortunately it is not possible to withdraw the whole of the liquid phase. It may be possible to determine the amount of liquid phase left behind in the reaction tube in the following manner. A small weighed amount of gold is added to the metals in the reaction tube. After the liquid

phase has been withdrawn a gold assay is made of the substance left behind in the tube. If it was known that all the gold passed into the liquid phase, the result of the gold assay would permit of the calculation of the amount of liquid phase left behind, and from this we should be able to determine the amount of solid which was in equilibrium with the total amount of liquid phase. Then by calculation the position could be found of the corresponding point on the solidus. This method we hope to test. It is possible that the solidus is more convex upwards than is represented in the figures. This point will be settled later on.

Discussion of the Results.

It is evident from inspection of the figures that all the diagrams are of the same type. The most striking feature is the rapid increase in size of the fields A and B with rise in temperature, so that at 166° the liquid field A, which at 63° reached less than one-tenth of the distance across the diagram towards the tin side, now reaches three-quarters of the way across.

Even more rapid is the falling off in the maximum content of tin in the solidus as the temperature is lowered; thus at 90° the solidus still extends about two-fifths of the distance across the diagram, but at 63°, only 27° lower, it reaches only one-sixth of this distance, and contains not more than just over 2 per cent. of tin. It is thus evident that at room temperature the tin capable of dissolving in the crystals of "*Arbor Dianae*," Ag_3Hg_4, must be quite negligible in amount, in accordance with the conclusions previously arrived at.

It will be evident from a comparison of Figs. 1—3 that an amalgam such as that represented by q, which is solid at room temperature, will partly liquefy at some temperature between 63° and 90°, and will gradually become more liquid as the temperature is raised. This seems to be a satisfactory explanation of the fact that breaks occur in the cooling curves. Although there is no reason for assuming the existence of two sets of equilibria, since the liquidus is of similar shape at all the temperatures investigated, yet for all practical purposes it remains true that we have to deal with a rapid change in the equilibria involved in most amalgams when these are heated through the temperatures lying between 70° and 100°.

The advance of the liquidus curve up the ternary diagram towards the Ag corner may be readily inferred from the way in which the solubility of silver in mercury increases with the temperature, together with the known behaviour of the binary liquids

on the Ag–Sn side of the diagram. This advance scarcely affects the type of equilibrium involved, and it is of no practical importance on account of the still more rapid increase in volatility of mercury.

The experiments arising out of this and the previous communications are being continued in this laboratory.*

Summary.

(1) The experimental data in a previous communication have been confirmed.

(2) Further experiments on the unique property of "ageing" have been described.

(3) The equilibrium diagrams have been extended to temperatures up to 214°. It has been shown that, although theoretically continuous throughout, for practical purposes they may be grouped into two classes—those above about 70° containing a large proportion of solid solution, those below containing negligible amounts only; thus the summarised equation of amalgamation at room temperature is:

$$Ag_3Sn + 4Hg \longrightarrow Ag_3Hg_4 + Sn.$$

The experiments presented above were commenced by one of us (R. A. J.) in 1910, and continued by the other throughout the present year. We desire to express our indebtedness to Dr. James W. McBain for constant advice throughout the investigation.

In conclusion our thanks are due to the Research Fund Committee of the Chemical Society for a grant towards the purchase of materials and apparatus.

THE CHEMICAL LABORATORY,
UNIVERSITY OF BRISTOL.

* Further experiments, which will be included in a later communication, have shown the hypothesis that ageing may be due to catalytic action of the iron or products of iron introduced during the filing to be untenable.

CCXXXV.—*The Influence of Solvents on the Rotation of Optically Active Compounds. Part XIX. The Rotation of Certain Derivatives of Lactic Acid.*

By THOMAS STEWART PATTERSON and WILLIAM COLLINS FORSYTH (Carnegie Research Scholar).

FROM the stereochemical point of view, lactic acid and its derivatives are of very considerable interest on account of the simple constitution of the molecule, especially, of course, the fact that it contains only one asymmetric carbon atom. We have thought it desirable, therefore, to prepare three of these derivatives of active lactic acid in order to examine their rotations through a fairly wide range of temperature, and also dissolved in two liquids, which, as experience has shown, differ greatly, as a rule, in their action.

Our optically active material was made by three different methods, which may be briefly indicated. The first consisted in resolving ordinary lactic acid by means of morphine (Irvine, T., 1906, **89**, 935). The syrupy lactic acid with which we commenced had a specific gravity of 1·21, and showed a slight positive rotation. By boiling this syrup with ten times its weight of water for six hours and then titrating with sodium hydroxide solution it was found that a quantity of lactic acid was formed, equal to 91·3 per cent. of the weight of the syrup. One hundred and ninety c.c. of this lactic acid were boiled under reflux with 2280 c.c. of water. To half of this solution 350 grams of morphine were added, whilst the other half—adopting a principle suggested by Pope and Peachey in the resolution of tetrahydroquinaldine (T., 1899, **75**, 1066)—was neutralised with the equivalent quantity, 46·3 grams, of sodium hydroxide. The solutions were mixed, and on cooling and then further evaporation three crops of crystals of morphine *l*-lactate were obtained, weighing in all 400 grams. The product was dissolved in 1100 c.c. of boiling water, and then an equal volume of alcohol added to the filtered solution. The substance which separated when the solution cooled was again crystallised in the same way, and ultimately a yield of about 83 per cent. of the theoretical was obtained. This is not quite so high as is recorded by Irvine, but it was obtained by the use of only half the proportional quantity of morphine. The pure morphine *l*-lactate was dissolved in hot water, the morphine precipitated by ammonia, and removed by filtration. Two-thirds of the filtrate were boiled with zinc oxide until the ammonia had all

disappeared, and, after filtration, the solution was added to the other third, the mixture being then concentrated by evaporation and set aside to crystallise, when zinc ammonium *l*-lactate was obtained. This had a rotation of $\alpha_D^{19.5}$ (100 mm.) 0·487°, $c = 8{\cdot}07$, which gives for the specific rotation +6·03°, whereas Purdie quotes +6·06° at 20°.

We also prepared active zinc ammonium lactate by the resolution of the zinc ammonium salt exactly according to Purdie and J. Wallace Walker (T., 1895, **67**, 618, 619; see also Purdie, T., 1893, **63**, 1143), and from 500 c.c. of lactic acid syrup 160 grams of zinc ammonium lactate were obtained. The specific rotation of this first crop of crystals was $[\alpha]_D^{20}$ +5·94°, $c=8$; α_D^{20} (200 mm.) 0·95°, so that the substance was practically pure, and on recrystallisation it gave $[\alpha]_D^{20}$ +6·05°. The yield thus obtained was rather more than three times that recorded by Purdie, and the mother liquor was found to have a rotation of +0·78° (100 mm.) at 20°, so that it still contained *l*-lactate in excess. The lactic acid with which this last experiment had been carried out was a different sample from that first used; it was obtained, through a local dealer, from Merck, and its rotation in a 100 mm. tube was found to be +4·36° at 20°, which is very much higher than the rotation usually found for ordinary lactic acid, and is considerably higher than the rotation of pure active lactic acid, this, of course being due to the fact that *l*-lactide is present, and has a high positive rotation. Commercial lactic acid often contains a slight preponderance of one or other of the active forms; but it is said to be only seldom that the *d*- or *l*-variety occurs in large excess (Meyer and Jacobson, "Lehrbuch der organischen Chemie," 2nd Ed., Vol. I., Part II, 560), and as this sample had so high an activity we thought it worth while to ascertain in what proportions the two constituents were present. Some of the acid was therefore converted into the ethyl ester by the method described by Purdie and Williamson (T., 1896, **69**, 828). This, after careful purification by distillation with a Sydney Young fractionating column under a pressure of 13 mm., boiled at 47—49°, and gave α_D^{18} (100 mm.) +4·5°, whilst Purdie and Williamson found the observed rotation of the pure ester at 14° to be 11·5°, and Purdie and Irvine (T., 1899, **75**, 485) found the observed rotation of their specimen at 8° to be 11·2°. The rotation of our preparation was therefore almost half that of the pure ester, so that the original lactic acid must have contained about 75 per cent. of *l*-acid and only 25 per cent. of *d*-acid (see Frankland and MacGregor, T., 1893, **63**, 1028; Harden, T., 1901, **79**, 610). We then obtained a number of samples of lactic acid from different sources

in order, if possible, to find another quantity with a high activity. As is well known, the rotation of lactic acid syrup itself is due chiefly to the presence of lactide, and in order to ascertain whether the rotation of the syrup is a good guide as to the quantity of active acid it contains we took 4 c.c. of each sample, placed it in a 50 c.c. flask, added to this 15 c.c. of a solution of 7 grams of sodium hydroxide in 45 c.c. of water, and then filled up to the mark with water. The rotation of the resulting solution of sodium lactate was then examined. The results were as follows:

Number of sample.	t.	Observed rotation of syrup (100 mm.).	Observed rotation of sodium salt solution (400 mm.).
1.	17·5°	+4·36°	+1·746°
2.	17·5	−0·65	−0·381
3.	17·5	+0·30	+0·164
4.	13·0	+5·30	+2·126

It will be noticed that the numbers for the rotation of the sodium salt solution are roughly proportional to those showing the rotation of the syrup, the rotations in both cases being of the same sign. It will be observed, further, that the last specimen showed an even higher rotation than that already referred to. We therefore obtained a quantity of this acid, which must have contained over 80 per cent. of *l*-lactic acid, and from it we prepared the zinc salt as follows: Three hundred grams, or 250 c.c., of the syrup were added to a mixture of 142 grams of zinc oxide and 3000 c.c. of hot water, and the whole boiled for some time until a neutral reaction was obtained. The liquid was decanted from a slight excess of zinc oxide, and allowed to crystallise. Inactive zinc lactate separated from the hot solution, and was collected. This preparation was repeated six times. The filtrate, on concentration, gave a deposit of active zinc lactate, which was crystallised several times, on each occasion from about six times its weight of boiling water, and in this way some 300 grams of pure zinc *l*-lactate were obtained with ease. If a fairly active specimen of lactic acid can be obtained, this is probably the simplest method of preparing an active salt. In the course of the crystallisation a considerable amount of partly active zinc lactate was obtained, from which zinc ammonium *l*-lactate was prepared. From 450 c.c. of the partly active lactic acid syrup and 250 grams of the partly active zinc lactate—which had a rotation of about 0·9° (400 mm.), $t = 13°$, $c = 1$; the pure salt would have α_D 1·4° in these circumstances—212 grams of pure active zinc ammonium *l*-lactate were obtained.

One difficulty which occurs in work on lactic acid is the fact that the rotation of its salts, such as the zinc and the zinc ammonium salts, is only low, and it is difficult, by using this criterion, to determine the purity of any sample with much accuracy. We

therefore adopted the plan of dissolving the salt in ammonia solution instead of in water. This had two advantages: in the first place, the zinc ammonium salt decomposes in water, separating out some less soluble zinc lactate, and this is prevented by the use of ammonia solution; in the second place, the presence of the ammonia considerably raises the rotation of the salt. Our ammonia solution was prepared by making up 300 c.c. of concentrated ammonia solution (D 0·880) to a litre with distilled water. The specific gravity of this solution by the Westphal balance was found to be 0·971, and the strength of the solution by titration with oxalic acid, using phenolphthalein as indicator, was 3·99*N*. Four grams of pure zinc ammonium lactate, made up to 50 c.c. with this solution, gave $\alpha_D^{17\cdot2}$(400 mm.) +3·232°, whereas the rotation in water was only 1·948°; thus by using ammonia solution the rotation is almost doubled.

Methyl l-*lactate* was prepared by the sulphuric acid method of Purdie and Williamson (T., 1896, **69**, 828) and Purdie and Irvine (T., 1899, **75**, 484), except that the crude ester was distilled through a Sydney Young fractionating column of 15 disks, under a pressure of about 13 mm., when it boiled at 40° and at 48°/ 16 mm. This is a considerable advantage, and saves the repeated and very wasteful distillation of the ester otherwise necessary. Methyl lactate, it may be noted, is fairly easily volatile along with methyl alcohol, the alcohol recovered in our first distillation (from an ordinary Wurtz flask) having a rotation of +0·36° (l = 400 mm.), and, when distilled with the column, gave a residue of 4 c.c. having a rotation of +4·2°, this quantity being, therefore, equivalent to 2 c.c. of the pure ester.

Rotation of Methyl l-*Lactate.*

The rotation of this preparation was then examined at various temperatures, with the following results:

$t°$	75·0	−62·0	−51·0	−8·6	+16·7	17·5
d	1·2042	1·1882	1·1752	1·1205	1·0971	1·0969
$\alpha_D^{t°}$ (100 mm.).	+6·596	6·726	6·861	8·396	8·882	8·95[illegible]
$[\alpha]_D^{t°}$	+5·479	5·661	5·838	7·45	8·10	8·17
$[M]_D^{t°}$...........	+5·696	5·887	6·071	7·75	8·42	8·49

$t°$	35·4	56·0	78·8	96·7	125·0
d	1·0751	1·0518	1·0256	1·0048	0·9725
$\alpha_D^{t°}$ (100 mm.) ...	9·332	9·808	10·238	10·536	10·824
$[\alpha]_D^{t°}$	8·68	9·32	9·98	10·48	11·13
$[M]_D^{t°}$	9·03	9·70	10·38	10·90	11·57

Methyl l-*Lactate in Nitrobenzene.*

The nitrobenzene had been distilled under diminished pressure.

$p = 9{\cdot}877$:

$t°$	16·0	18·9	36·2	37·9	56·5	81·9	104·5	141·0
$d^{t°}_{4°}$	1·1920	1·1910	1·1735	1·1717	1·1525	1·1270	1·1021	1·0670
$\alpha^{t°}_D$ (62 mm.)	+1·856	1·876	1·836	1·846	1·850	1·856	1·850	1·846
$[\alpha]^{t°}_D$	9·854	9·947	9·902	9·98	10·16	10·42	10·63	10·95
$[M]^{t°}_D$	10·24	10·35	10·30	10·38	10·56	10·84	11·05	11·39

Methyl l-*Lactate in Tetrachloroethane (Acetylene Tetrabromide).*

The tetrachloroethane was distilled under 13 mm. pressure, and boiled at 115—117°.

$p = 9{\cdot}937$:

$t°$	−7·8	+17·6	39·7	69·8	91·3	120
$d^{t°}_{4°}$	2·5825	2·5292	2·4840	2·4220	2·3706	2·3160
$\alpha^{t°}_D$ (100 mm.)...	−3·146	−1·903	−0·998	−0·032	+0·738	+1·376
$[\alpha]^{t°}_D$	−7·66	−4·73	−2·53	−0·083	+1·96	+3·74
$[M]^{t°}_D$	−7·97	−4·92	−2·63	−0·086	+2·04	+3·89

Methyl l-*a-acetoxypropionate* was prepared by boiling methyl l-lactate with excess of acetyl chloride. The product of the reaction was distilled under diminished pressure, using a Sydney Young column. It boiled at 68—70°/13 mm. and 171—172° at atmospheric pressure.

Rotation of Methyl l-*a-Acetoxypropionate.*

$t°$	7·4	+19·8	43·0	59·5	83·2	114·6	141·0
$d^{t°}_{4°}$	1·1199	1·0885	1·0620	1·0435	1·0165	0·9808	0·9500
$\alpha^{t°}_D$ (50 mm.)	+30·394	29·552	28·78	28·224	27·448	26·514	25·694
$[\alpha]^{t°}_D$	54·26	54·28	54·20	54·09	54·03	54·05	54·08
$[M]^{t°}_D$	79·23	79·25	79·14	78·98	78·89	78·93	78·96

Methyl l-*a-Acetoxypropionate in Nitrobenzene.*

$p = 10{\cdot}14$:

$t°$	0·3	19·2	45·4	65·0	83·5	110·0	141·0
$d^{t°}_{4°}$	1·2105	1·1919	1·1650	1·1445	1·1262	1·10	1·0690
$\alpha^{t°}_D$ (100 mm.)	+7·336	6·914	6·364	6·126	5·908	5·708	5·514
$[\alpha]^{t°}_D$	+59·78	57·20	53·88	52·77	51·76	51·18	50·88
$[M]^{t°}_D$	+87·30	83·52	78·66	77·05	75·58	74·73	74·29

Methyl l-*a-Acetoxypropionate in Tetrachloroethane.*

$p = 10{\cdot}035$:

$t°$	17·6	39·8	54·7	76·4	91·3	119·0	139·3
$d^{t°}_{4°}$	2·5262	2·4817	2·4520	2·4078	2·3772	2·3220	2·2705
$\alpha^{t°}_D$ (100 mm.)	+19·294	18·886	18·632	18·234	18·066	17·722	17·428
$[\alpha]^{t°}_D$	+47·56	47·37	47·32	47·17	47·34	47·53	47·80
$[M]^{t°}_D$	+69·45	69·18	69·08	68·87	69·11	69·40	69·81

Methyl l-*α-methoxypropionate* was prepared exactly according to the method of Purdie and Irvine (T., 1899, **75**, 485), and was finally distilled with a column, under diminished pressure. It boiled at 40°/18 mm. and 130—131°/760 mm.

Rotation of Methyl l-*α-Methoxypropionate.*

$t°$	−16·6	16·4	41·2	51·1	78·4	110·0	130·6
d	1·0361	0·9986	0·9704	0·9590	0·9283	0·8916	[illegible]
α_D^{t} (30 mm.)	+32·107	29·112	27·28	26·414	24·528	22·826	[illegible]
$[\alpha]_D^{t}$	+103·3	97·16	93·71	91·81	88·28	85·35	[illegible]
$[M]_D^{t}$	+121·9	114·7	110·6	108·3	104·2	100·7	[illegible]

Methyl l-*α-Methoxypropionate in Nitrobenzene.*

$p = 9·802$:

$t°$	16·6	41·7	70·5	92·8	119·0
d	1·1843	1·1590	1·1290	1·1066	1·0795
α_D^{t} (160 mm.)	+16·496	15·55	14·544	13·756	12·925
$[\alpha]_D^{t}$	+88·82	85·27	82·17	79·25	76·40
$[M]_D^{t}$	+104·8	100·7	97·18	93·53	90·36

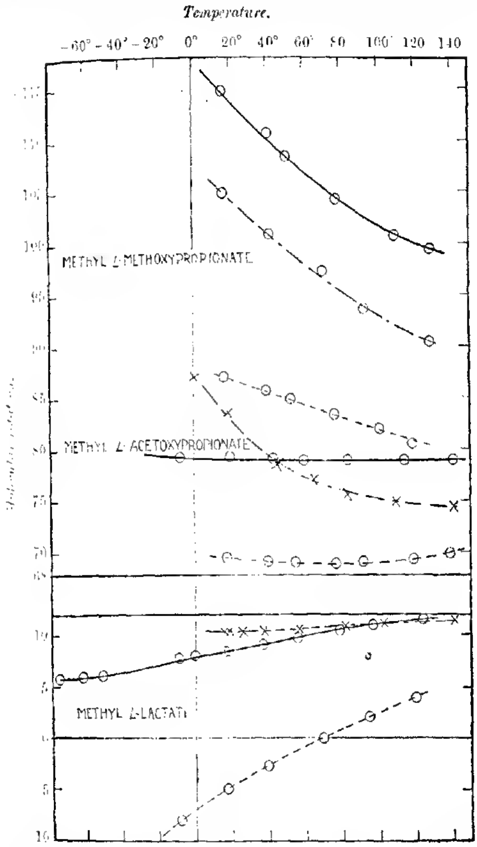
Methyl l-*α-Methoxypropionate in Tetrachloroethane.*

$p = 10·0616$:

$t°$	16·7	39·8	52·5	77·0	101·0	119·6
d	2·4860	2·4390	2·4135	2·3630	2·3140	[illegible]
α_D^{t} (100 mm.)	+18·444	17·798	17·448	16·766	16·156	[illegible]
$[\alpha]_D^{t}$	+73·69	72·52	71·85	70·52	69·40	[illegible]
$[M]_D^{t}$	+86·96	85·59	84·78	83·22	81·91	[illegible]

The diagram represents our experimental data. The relative rotations of methyl *l*-lactate, methyl *l*-*α*-acetoxypropionate, and methyl *l*-*α*-methoxypropionate at a single temperature were, of course, already known, but the influence of temperature change on them has not previously been studied. The full lines in the diagram represent the behaviour of the homogeneous active substances, and it will be observed that the influence of temperature change in the three cases is comparatively slight; thus the rotation of methyl *l*-lactate only changes some 6° within a temperature range of fully 200°; nevertheless, the curve has two interesting characteristics. First, at the higher temperatures it tends, apparently, towards a maximum value, and second, since there appears to be a point of inflexion somewhere about −10°, it is possible that at lower temperatures than those we have reached, a minimum rotation also may exist for methyl *l*-lactate. The importance of maximum and minimum rotations and points of inflexion has been discussed by one of us in a recent paper (this vol., p. 145), so that the matter need not be further dealt with here.

When methyl *l*-lactate is converted into methyl *l*-α-acetoxypropionate the change is accompanied by a great rise of rotation, but the rotation of the acetyl compound is very little affected by



Temperature-rotation curves for derivatives of l-*lactic acid in the homogeneous condition* (full lines), *in solution in nitrobenzene*, p = 10 (dash-dash-dot curves), *and in tetrabromoethane*, p = 10 (dotted curve).

change of temperature within the ordinary limits. A minimum rotation appears to exist, however, at a temperature in the neighbourhood of 40°, and this accounts for the comparative invaria-

bility of the rotation with change of temperature, since it is, of course, in the neighbourhood of a maximum or a minimum that $d\alpha/dt$ is a minimum.

When the acetoxy-group is replaced by a methoxy-group a compound is obtained which has a still higher rotation, a rotation which diminishes fairly rapidly with rise of temperature. Now it has been suggested in the paper already referred to (*loc. cit.*) that the temperature-rotation curves for a set of closely-related compounds such as these may all be of the same type, the exchange of certain groups for others merely producing a shift of the fundamental type of curve to the right or the left, to the top or bottom of the diagram, accompanied, however, by individual but minor differences and characteristics. It is thus possible that the minimum which occurs in the rotation of methyl *l*-lactate at a low temperature of about $-80°$ or $-100°$ represents a condition of the molecule corresponding with that which is assumed by methyl *l*-α-acetoxypropionate at a temperature of $+40°$ and in methyl *l*-α-methoxypropionate at a temperature in the neighbourhood of 200°, and this affords some explanation of the fact that whilst the rotation of methyl lactate increases on heating, that of methyl *l*-α-acetoxypropionate is but little altered, and that of methyl *l*-α-methoxypropionate diminishes.

The rotation of each of these active compounds was also examined in nitrobenzene and in tetrabromoethane solution. Previous work with ethyl tartrate had shown that whereas nitrobenzene has a very pronounced effect in raising the rotation of ethyl tartrate, tetrabromoethane is almost equally powerful in diminishing it. Therefore, it appeared to be of interest to ascertain in what way the rotation of these other active compounds would be influenced by the same two solvents. In the case of methyl *l*-lactate it seems tolerably clear that in nitrobenzene solution the minimum rotation would occur at a higher temperature than in the homogeneous ester. It is probable also that a maximum rotation would exist in this same solution, but the curves are not sufficiently extensive to decide whether at a higher or a lower temperature than in the homogeneous ester. A point of inflexion is indicated at about 60°.

Nitrobenzene as a solvent does not produce so great an elevation of the rotation of methyl *l*-lactate as of that of ethyl tartrate, and similarly tetrabromoethane, although it considerably diminishes the rotation of the lactate, does so to a less extent than in the case of ethyl tartrate. No point of inflexion is apparent in this curve, so that a minimum rotation would be expected to occur at a still lower temperature than in the homogeneous ester. From the curves it is hardly possible to say whether the maximum rotation

of this solution will lie at a lower temperature than that of the homogeneous ester or of the ester dissolved in nitrobenzene.

The influences of nitrobenzene and of tetrabromoethane on the rotation of methyl *l*-α-methoxypropionate are, on the whole, somewhat similar to their effects on the rotations of the other two esters examined. Tetrabromoethane brings about the greater lowering of rotation, but the nitrobenzene curve does not cut that for the homogeneous ester. We may point out, however, although it may seem to be arguing on somewhat slender premisses, that whereas the curve for the homogeneous ester and that in nitrobenzene solution for methyl *l*-lactate occurs at a fairly high temperature of about 100°, a similar intersection takes place for methyl *l*-α-acetoxypropionate at about 40°, and therefore it may possibly be that a corresponding intersection in the case of methyl α-methoxypropionate should occur at a still lower temperature. For this ester also it may be noticed that the three curves are more widely separated from each other, thus suggesting that as the rotation of the compound becomes greater the sensitiveness of the molecular asymmetry to the influences of different solvents becomes greater also; in other words, the change produced in passing from one solvent to another is greater for the methyl *l*-α-methoxypropionate with its high rotation than for the methyl *l*-lactate with its low rotation. The three curves in this case appear to be tending towards a minimum value, but it is obviously difficult or impossible to say what the relative position of these minima would be.

The effect of the two solvents is much the same on the three different esters, thus supporting the view, which is steadily gaining ground, that the relative influence of a set of solvents on several active compounds is closely similar.

On the whole, it may be said that these curves, although perhaps they do not present any very striking confirmation or support of the ideas suggested in the paper referred to, are quite in harmony with these suggestions. It is a little unfortunate that the comparatively easy volatility of the substances examined has somewhat limited their investigation.

In conclusion, we have to thank Messrs. T. and H. Smith, of Edinburgh, for the loan of a considerable quantity of morphine and for presenting us with another quantity of it for use in the experiments recorded, whilst we desire also to acknowledge that some of the rotation data quoted in the paper were obtained with a polarimeter placed at the disposal of one of us by the Carnegie Trustees for the Universities of Scotland.

ORGANIC CHEMISTRY DEPARTMENT,
UNIVERSITY OF GLASGOW.

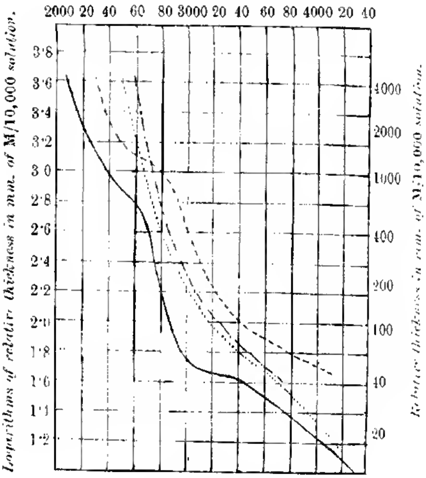
CCXXXVI.—*The Tautomerism of Thioanilides.*

By Percy May.

In order to decide which of the two possible tautomeric formulæ better represents thiobenzanilide itself, the two methyl derivatives have been examined and their properties compared with those of the parent substance.

The absorption curve of the parent substance closely resembles

Fig. 1.



that of the *N*-methyl derivative (I). The curves for the sodium salt and the *S*-methyl derivative (II) are practically identical, but differ in character from, and show less general absorption* than, those of the parent substance and *N*-methyl derivative.

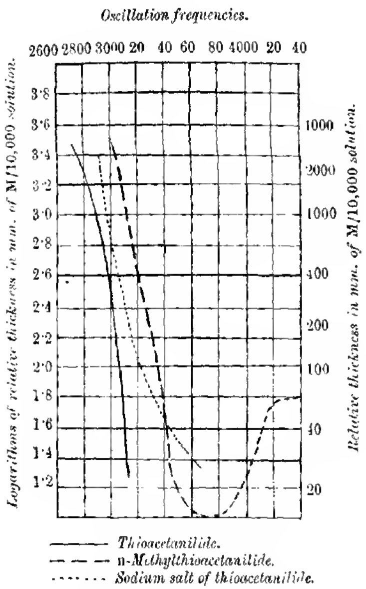
$$\underset{\text{(I.)}}{C_6H_5\cdot\underset{|}{\overset{}{N}}(CH_3)\text{——}\underset{||}{C}(S)\cdot C_6H_5}\qquad\qquad \underset{\text{(II.)}}{C_6H_5\cdot N:\underset{|}{C}(S\cdot CH_3)\cdot C_6H_5}$$

* In comparing the general absorption, only the upper portion of the curves, where there are neither bands nor incipient bands, is considered.

The spectroscopic evidence, therefore, is in favour of the usual thioketone formula for thiobenzanilide.

On the other hand, the sodium salt and *S*-methyl derivative (III) of thioacetanilide show greater general absorption than the *N*-methyl derivative (IV). This is in accordance with the observation that substances containing double bonds in the conjugated

FIG. 2.



position show greater general absorption than isomeric compounds containing the double bonds in the unconjugated position:

$$\begin{array}{c} C_6H_5\cdot N{:}\underset{\displaystyle S\cdot CH_3}{\underset{|}{C}}\cdot CH_3 \\ \text{(III.)} \end{array} \qquad \begin{array}{c} C_6H_5\cdot\underset{\displaystyle CH_3}{\underset{|}{N}}\text{——}\underset{\displaystyle S}{\underset{||}{C}}\cdot CH_3 \\ \text{(IV.)} \end{array}$$

In the case of thioacetanilide, the spectroscopic evidence is not very conclusive, but here also it appears to favour the thioketone structure.

On attempting to methylate thiobenzanilide in neutral solvents decomposition always took place, the sulphur being eliminated as

methyl sulphide. When the reaction was carried out in hot xylene solution the chief product of the reaction was sulphanilic acid. The small amount of water present in the solvent brings about this complete decomposition, which probably takes place in two stages:

$$C_6H_5{\cdot}NH{\cdot}CS{\cdot}C_6H_5 + (CH_3)_2SO_4 + H_2O = C_6H_5{\cdot}NH{\cdot}CO{\cdot}C_6H_5 + (CH_3)_2S + H_2SO_4.$$

$$C_6H_5{\cdot}NH{\cdot}CO{\cdot}C_6H_5 + H_2SO_4 = HSO_3{\cdot}C_6H_4{\cdot}NH_2 + C_6H_5{\cdot}CO_2H$$

In some solvents the first stage, formation of methyl sulphide, is complete at room temperature.

Experimental.

S-*Methylthiobenzanilide* was obtained as a white, crystalline precipitate on adding an excess of methyl sulphate to a solution of thiobenzanilide in aqueous sodium hydroxide. On crystallisation from aqueous alcohol it separates in colourless, fine needles, melting at 63—64°. It is almost insoluble in cold water or alkali, but readily soluble in most organic solvents:

0·1350 gave 0·3640 CO_2 and 0·0717 H_2O. C=73·53; H=5·90.

$C_{14}H_{13}NS$ requires C=73·94; H=5·77 per cent.

Action of Methyl Sulphate on Thiobenzanilide in Neutral Solvents.

Methyl sulphate readily reacts with thiobenzanilide in neutral solvents, such as benzene, xylene, nitrobenzene, or methyl alcohol; for example, 5 grams of thiobenzanilide were dissolved in xylene, and 5 grams of methyl sulphate added. A red colour was produced, and on warming a rapid evolution of methyl sulphide occurred, and a solid separated. This was collected, purified, and recrystallised from hot water, and was then identified as sulphanilic acid (Found, after drying at 120°, C=41·3; H=4·55. M.W.=174. $C_6H_7O_3NS$ requires C=41·6; H=4·05 per cent. M.W.=173.)

Methyl sulphide is also formed when the reaction is carried out in the other solvents mentioned above, and when methyl iodide reacts with a methyl-alcoholic solution of thiobenzanilide.

N-*Methylthiobenzanilide.*

Methylbenzanilide was obtained by the action of benzoyl chloride on a pyridine solution of methylaniline, and was finally obtained in large, transparent crystals melting at 58°. Four grams of phosphorus pentasulphide, 2 grams of phosphorus trisulphide, and 6 grams of methylbenzanilide were powdered, mixed, and heated for half-an-hour on the water-bath. The product was extracted

with ether, and the crude substance so obtained extracted with cold alcohol, which dissolved out some dark-coloured impurities. The residue was crystallised from ether, and recrystallised from aqueous alcohol, from which it separates in small, yellow cubes, melting at 90—91°:

0·1455 gave 0·1570 $BaSO_4$. S = 14·52.

$C_{14}H_{13}NS$ requires S = 14·11 per cent.

My thanks are due to the Research Fund Committee of the Chemical Society for a grant towards the expenses of the investigation, and to Dr. Smiles, who kindly supplied me with the thiobenzanilide.

UNIVERSITY OF LONDON,
UNIVERSITY COLLEGE.

CCXXXVII.—*Mechanism of the Decomposition of Carbamide and Biuret by Heat, and of the Formation of Ammelide.*

By EMIL ALPHONSE WERNER.

IN continuation of the work recently published (this vol., p. 1010), further experiments have now been completed, the results of which afford a full explanation of the mechanism of the different changes under consideration, and supply further evidence in support of the theories which have been put forward by the author.

Considering the number of communications which have appeared from time to time on the decomposition of carbamide by heat, it is rather remarkable that no careful quantitative study of the changes appears ever to have been made; to supply this want, and to clear up certain undoubtedly misleading statements on record, the present investigation was carried out.

It has been shown (*loc. cit.*) that when pure dry carbamide is heated slightly above its melting point it undergoes rapid dissociation, ammonia and cyanic acid being formed as sole volatile products, in accordance with the equation:

$$HN{:}C\begin{matrix}\diagup NH_3 \\ | \\ \diagdown O\end{matrix} = \begin{matrix} NH_3 \\ + \\ HOCN \rightleftharpoons HN{:}CO\end{matrix}.$$

Cyanuric acid is produced as a result of the polymerisation of a portion of the cyanic acid originally present in the keto-form,

whilst biuret is simultaneously formed by the action of cyanic acid on unchanged carbamide, further evidence of which has been obtained from the study of the action of heat on biuret, described later on. If the heating is prolonged, and particularly if the temperature is raised to 190—200°, a small quantity of ammelide is formed, the production of which has been recognised for a long time by different observers, although no importance apparently has been attached to its existence as a product of the decomposition of carbamide by heat. It will be shown, however, in the following that the formation of ammelide has an interesting significance when dealing with the explanation of the mechanism of the different changes, and its production calls for immediate comment before giving the detailed results of the quantitative study of the whole process.

Some years ago Hantzsch and F. Hofmann (*Ber.*, 1905, 38 1013) examined the action of heat on carbamide, and whilst they showed that no cyamelide is formed, they obtained a sparingly soluble substance resembling the latter in appearance, which they concluded to be tricyanocarbamide, $C_3N_3(NH \cdot CO \cdot NH_2)_3$, the possibility of the substance being ammelide was apparently overlooked, in spite of the fact that all the properties of the compound as described by Hantzsch are in agreement with that substance. After a careful investigation of the substance, the details of which are given in the experimental part of the paper, the author is forced to the conclusion that no such substance as tricyanocarbamide is produced by the action of heat on either carbamide or biuret, ammelide alone being the very sparingly soluble substance which is formed in both cases, and the origin of its production will be dealt with under the decomposition of biuret.

I. *Quantitative Study of the Decomposition of Carbamide by Heat.*

The general plan adopted in all the experiments was as follows: Five grams of pure dry carbamide were heated in a thin-walled test-tube, 18 cm. long by 2·5 cm. wide; whilst the tube was maintained in a nearly horizontal position, the heat was applied directly with a small flame. After removal of the sublimate, the residue was thoroughly extracted with cold water to the volume of 100 c.c.: the biuret formed was estimated colorimetrically in an aliquot portion of the solution by the aid of the well-known "biuret reaction"; this was found to give very satisfactory results, even in the presence of cyanuric acid and carbamide. The residue from the aqueous extract was dried and weighed, the total cyanuric acid present in this residue and in the aqueous solution was

estimated by titration with $N/10$-sodium hydroxide solution, as described in a previous paper (*loc. cit.*), and the ammelide was determined by difference, or in some cases by direct weighing after removal of the cyanuric acid by solution in warm water.

The results of four experiments are given below:

TABLE I.

	Expt. I. Heated very slowly; heat stopped as soon as opalescence set in. Time, 12 minutes. Per cent.	Expt. II. Heated at a moderate rate until appearance of opalescence. Time, 7—8 minutes. Per cent.
Loss (NH_3 + HCNO)	8·40	12·20
NH_4OCN (in sublimate)	0·58	0·21
Biuret	18·26	24·50
Cyanuric acid	3·35	5·93
Ammelide	0·83	3·94
	31·42	46·78
Unchanged carbamide (by difference)	68·58	53·22

	Expt. III. Heated rather rapidly until appearance of opalescence. Time, 5 minutes. Per cent.	Expt. IV. Heated very rapidly; heat continued, after appearance of opalescence, until gas evolution had practically ceased. Time, 6—7 minutes. Per cent.
Loss	15·00	19·00
NH_4OCN	0·06	0·42
Biuret	16·66	10·25
Cyanuric acid	9·16	15·34
Ammelide	3·30	8·46
	44·18	53·47
Unchanged carbamide (by difference)	55·82	46·53

In experiments I and II the temperature did not rise beyond 190°; in III and IV the temperature reached 205° as a maximum, but was most of the time about 195°.

The following results represent the proportions of biuret and cyanuric acid respectively, calculated on the amount of carbamide actually decomposed in each experiment:

TABLE II.

	Expt. I.	Expt. II.	Expt. III.	Expt. IV.
Biuret	58·1	52·4	37·7	19·1 per cent.
Cyanuric acid	10·6	12·7	20·7	28·6 ,, ,,

Thus slow heating at a temperature well below the melting point (?) of biuret represents the best conditions for the production of this substance, which is in agreement with the view already given regarding the theory of its formation; rapid heating, as

might naturally be expected, hastens the polymerisation of cyanic acid, a factor which militates against biuret formation.

II. *Quantitative Study of the Decomposition of Biuret by Heat.*

The decomposition of biuret by heat is generally disposed of by the simple statement that it gives off ammonia and yields cyanuric acid; whilst this even is only partly true, the primary action of heat on biuret, which is of particular interest, appears to have been hitherto quite overlooked.

It has been recently pointed out by the author (*loc. cit.*) that when biuret is heated in a test-tube to the point of decomposition, it furnishes a crystalline sublimate composed of carbamide and ammonium cyanate, thus proving that cyanic acid must accompany the ammonia as a volatile product. It is now shown, from the results recorded below, that the first effect of the action of heat on biuret just above its melting point is to cause its dissociation into the products from which it was generated, namely, carbamide and cyanic acid, from which it follows that the formation of biuret, during the action of heat on carbamide, is a reversible change, in accordance with the equation:

$$HN{:}C\Big\langle{}^{NH_2}_{OH} + HN{:}CO \underset{\text{above }190^\circ}{\overset{135-190^\circ}{\rightleftarrows}} \underset{\text{Biuret (enol-form).}}{\begin{array}{c}HN{:}C\cdot OH^*\\ | \\ NH \\ | \\ HN{:}C\cdot OH\end{array}} \rightarrow \underset{\text{(Keto-form).}}{\begin{array}{c}O{:}C\cdot NH_2\\ | \\ NH \\ | \\ O{:}C\cdot NH_2\end{array}}$$

Since carbamide is regenerated at a temperature considerably above the limit of its stability, it dissociates rapidly into ammonia and cyanic acid, the latter quickly polymerising; this prevents a state of equilibrium, corresponding with the above equation, from persisting for any length of time; nevertheless, by heating biuret for a few minutes just above its melting point, and afterwards cooling rapidly, as much as 30 per cent. of carbamide may be readily extracted from the residue. Ammelide is also formed during the decomposition of biuret,† and, as will be presently shown, the latter is, in fact, a necessary precursor to the formation of ammelide during the decomposition of carbamide. Before dealing with the theory of its origin, the quantitative results of the action of heat on biuret are given in the following table.

Four grams of anhydrous biuret were used in each experiment.

* The above change being established, it is obvious that the question of the constitution of biuret is opened up thereby; this matter, together with the constitution of carbamide, is at present under investigation, and the results shall form the subject of a future communication.

† This has already been noticed by Hantzsch (*loc. cit.*), although he has considered the substance to be tricyanocarbamide.

…imation of the products formed was carried out as …nder carbamide; the numbers given below represent … of the weight of biuret taken.

TABLE III.

	Expt. I. …eated at 195—198° …d pasty mass formed. Time, 5 minutes.	Expt. II. Heated until gas evolution ceased (195—200°). Time, 7 minutes.	Expt. III. Heated rapidly (195–205°) until residue solid. Time, 10 minutes.
… (NH_3 + HNCO)	8·25 per cent.	13·75 per cent.	23·12 per cent.
[illegible]	4·95 ,,	6·37 ,,	3·75 ,,
… acid	37·24 ,,	37·08 ,,	57·96 ,,
[illegible]	3·57 ,,	5·87 ,,	5·37 ,,
… (unchanged)	12·34 ,,	10·40 ,,	0·77 ,,
	66·35 ,,	73·47 ,,	90·97 ,,
… generated	33·65 ,,	26·53 ,,	9·03 ,,

The carbamide was not directly determined, but its presence in quantity was proved by precipitation as nitrate, and by other tests, … a portion of the aqueous extract of the residues from experiments I and II. The following experiment was made with the main object of determining the carbamide formed.

Eight grams of biuret were heated, in a short, wide-mouthed …e immersed in a bath of glycerol, for ten minutes at 192°. The …rbamide was estimated by precipitation as nitrate; whilst this …s bound to give a result below the real value, it was sufficiently accurate for the purpose required. The residue after heating was extracted with 30 c.c. of cold water; 20 c.c. of this solution gave on addition of 15 c.c. of concentrated colourless nitric acid 2·88 grams of carbamide nitrate, the composition of which was checked by titration with N-sodium hydroxide solution.

Results Obtained.

Expt. IV.

Carbamide	26·42	per cent.
Cyanuric acid	24·85	,,
Ammelide	2·88	,,
Biuret (unchanged)	22·40	,,
	76·55	

Neither the sublimate nor the loss by volatilisation was determined. As already pointed out in the case of carbamide, rapid heating largely increases the yield of cyanuric acid by hastening polymerisation of the cyanic acid set free; this is not accompanied by any increase in the amount of ammelide formed, the maximum yield of which is probably reached under the conditions of expt. II, table III, so far as the decomposition of biuret is concerned.

When anhydrous biuret is heated, the evolution of a small quantity of aqueous vapour is noticeable as soon as decomposition sets in, a phenomenon which is not observable in the case of carbamide until the temperature reaches about 155°, below which no ammelide is formed. The evolution of water is, in fact, a by-product of the formation of ammelide, which, the facts seem to indicate, originates from the interaction of biuret and cyanic acid in accordance with the equation:

$$\mathrm{HN}\!<\!\begin{matrix}\mathrm{CO\cdot NH_2}\\ \mathrm{CO\cdot NH_2}\end{matrix} + \mathrm{HN{:}CO} = \mathrm{HN}\!<\!\begin{matrix}\mathrm{CO\cdot NH}\\ \mathrm{CO\cdot NH}\end{matrix}\!>\!\mathrm{C{:}NH} + \mathrm{H_2O}.$$

Ammelide.*

Another explanation of its origin might be found in its possible formation as a result of the direct interaction of ammonia and cyanuric acid, thus:

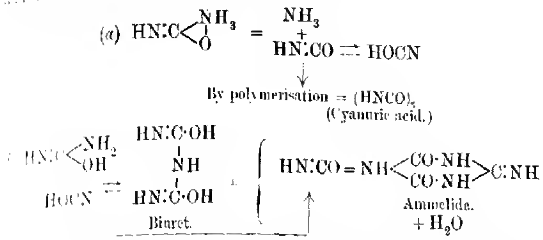
$$\mathrm{HN}\!<\!\begin{matrix}\mathrm{CO\cdot NH}\\ \mathrm{CO\cdot NH}\end{matrix}\!>\!\mathrm{CO} + \mathrm{NH_3} = \mathrm{HN}\!<\!\begin{matrix}\mathrm{CO\cdot NH}\\ \mathrm{CO\cdot NH}\end{matrix}\!>\!\mathrm{C{:}NH} + \mathrm{H_2O}.$$

A direct experiment to test this gave a negative result, no ammelide being formed by heating cyanuric acid to 160—180° in a current of ammonia. Moreover, since ammonia is continuously evolved during the decomposition of biuret, an increase in the yield of ammelide might naturally be expected to accompany an increase in the production of cyanuric acid; this, however, is not the case, as shown in expt. III, table III; on the contrary, all other conditions being equal, rapid removal of the biuret from the sphere of action is accompanied by a fall in the yield of ammelide, which is in agreement with the theory of its formation given above. This also explains why a much larger quantity of ammelide is formed by the action of heat on carbamide, under suitable conditions, as compared with the action of heat on biuret; this is well shown in the results of expt. IV, table I, where the yield of ammelide was equal to 15·8 per cent. of the weight of carbamide decomposed. In accordance with the theory of its formation it is obvious that the yield of ammelide cannot be other than small, since the temperature at which it appears to be most rapidly formed lies about the point at which biuret is rapidly decomposed and at which cyanic acid undergoes very rapid polymerisation.

Thus the mechanism of the series of changes which accompany the progressive action of heat on carbamide may be illustrated by the following scheme, in which it is seen that the phenomenon of

* This is the tautomeric form of $\mathrm{HN}\!<\!\begin{matrix}\mathrm{CO\cdot NH}\\ \mathrm{CO{-}N}\end{matrix}\!>\!\mathrm{C\cdot NH_2}$, which is also used to express the constitution of ammelide, since this substance possesses feeble basic, in addition to pronounced acidic, properties.

... and the instability and reactivity of nascent cyanic ... the active agents in the process:



Whilst the cyclic formula (*a*) is used to represent the constitution of carbamide in the first stage of the decomposition, it is ... unlikely that the direct dissociation of carbamide into ammonia and cyanic acid by heat is also accompanied by a change in constitution represented by the hydroxylic formula (*b*); this alteration in structure would probably be determined by the presence of a negative agent, such as cyanic or cyanuric acid in the fused product.

Experimental.

Preparation and Identification of Ammelide.

Before any definite conclusions could be drawn from the experimental results, it was necessary to place beyond doubt the nature of the sparingly soluble substance formed in the experiments described, since Hantzsch (*loc. cit.*) has described as tricyanocarbamide, $C_3N_3(NH{\cdot}CO{\cdot}NH_2)_3$, a product having all the characteristics of ammelide.

The opalescence which suddenly appears in the fused product after carbamide has been heated for a short time above 150° is due to the separation of this substance; it was readily freed from the other products by extracting the latter with warm water. Nitrogen estimations were made in four different preparations, with the following results:

(*a*) From action of heat on carbamide. No purification beyond thorough extraction with warm distilled water:

0·198 gave 73·7 c.c. N_2 at 15° and 768·5 mm. N=44·29.

(*b*) Same as (*a*). Purified by crystallisation from hot 5 per cent. hydrochloric acid solution:

0·1475 gave 54·9 c.c. N_2 at 18° and 763 mm. N=43·38.

(*c*) Same as (*a*). Purified by dissolving in sodium hydroxide solution, and, after filtration, precipitating with acetic acid:

0·1065 gave 39·9 c.c. N_2 at 17° and 766·5 mm. N=43·78.

(*d*) From action of heat on biuret. Purified as in (*c*).

0·1365 gave 50·9 c.c. N_2 at 17° and 769 mm. N=43·8[illegible]

$C_3H_4O_2N_4$ (ammelide) requires N=43·75 per cent.

$C_6H_9O_3N_9$(tricyanocarbamide) requires N=49·41 per cent.

Hydrolysis of the compound gave the following results:

0·5 Gram heated with 15 per cent. hydrochloric acid for two hours at 140—150° in a sealed glass tube was completely hydrolysed with formation of ammonia and cyanuric acid as the sole products; no carbamide was formed, and there was no evolution of carbon dioxide on opening the tube. The change is in agreement with the equation:

$$C_3H_4O_2N_4 + H_2O = C_3H_3O_3N_3 + NH_3,$$

and proves, together with the analytical results, that the very sparingly soluble substance formed in all the experiments is ammelide only.

Colorimetric Estimation of Biuret.

This was carried out in the following manner: A standard solution of convenient strength was prepared by dissolving 0·5 gram of pure anhydrous biuret in about 200 c.c. of distilled water, to which 50 c.c. of *N*-sodium hydroxide solution were added; freshly precipitated copper hydroxide * was then introduced, until, after thorough shaking, a small quantity of the hydroxide remained undissolved; the solution was then diluted with distilled water to 500 c.c., well mixed, and allowed to remain until the slight excess of copper hydroxide had completely subsided. The clear, purple-red solution so obtained could then be removed by means of a pipette as required; 25 c.c. (=0·025 of biuret), diluted with water to 100 c.c. in a Nesslerising cylinder, were found to give a suitable colour tint for comparison with the solutions obtained from the present experiments.

The results of two check experiments will suffice to give an idea of the accuracy which may be obtained in the estimations:

A. Biuret(present in 100 c.c. of solution)=0·095. Found=0·09448.

B. Biuret(with equal weights of carbamide and cyanuric acid also present in solution)=0·175. Found=0·1739.

UNIVERSITY CHEMICAL LABORATORY,
TRINITY COLLEGE, DUBLIN.

* Prepared by adding a slight excess of sodium hydroxide to copper sulphate solution, without any further treatment.

CCXXVIII.—*The Absorption Spectra of Various Derivatives of Pyridine, Piperidine, and Piperazine in Solution and as Vapours.*

By JOHN EDWARD PURVIS.

The absorption spectra of solutions of pyridine, α- and β-picolines, and piperidine have been studied by Hartley (T., 1885, **47**, 685), and by Baker and Baly (T., 1907, **91**, 1122), and they found one large band in pyridine and α- and β-picolines, but none in piperidine.

The author has given accounts of the absorption spectra of the vapours and alcoholic solutions of pyridine and some of its derivatives (*Proc. Camb. Phil. Soc.*, 1907, **14**, 381; 1908, **14**, 436, 568; T., 1909, **95**, 294). It was proved that whereas the vapours of pyridine and α-picoline exhibit a considerable number of fine, narrow bands, the vapours of 2:6- and 2:4-dimethylpyridines and 2:4:6-trimethylpyridine showed none of these finer bands, and that there was only a single large absorption band comparable with the solution band. It was also shown that the vapour of piperidine had a considerable number of fine, narrow bands, although the solution had none.

The vapours of several of the substances then examined have since been investigated, and also the solutions and vapours of other derivatives of pyridine, piperidine, and piperazine. These substances were: 2-dipyridyl (solution and vapour); 4-phenylpyridine (solution and vapour); 3:5-dichloropyridine (vapour); 2:3:5-trichloropyridine (vapour); 3:4:5-trichloropyridine (vapour); 2:3:4:5-tetrachloropyridine (vapour); tetrachloro-2-aminopyridine (vapour); pentachloropyridine (vapour); methyl trichloropicolinate (vapour); 2:3:4-trichloropicolinamide (vapour); 2:3:4-hexachloropicoline (vapour); piperidine (neutral and acid solutions); 4-phenylpiperidine (solution and vapour); nitrosopiperidine (solution and vapour); benzoylpiperidine (solution and vapour); and piperine (vapour). The solutions of a number of these substances have been examined before (*loc. cit.*), so that their vapours only were now investigated. The piperazine substances examined were: piperazine (solution and vapour); α- and β-dimethylpiperazines (solution and vapour); dibenzoyl-α- and β-dimethylpiperazines (solutions).

The apparatus and methods of working have been described before.

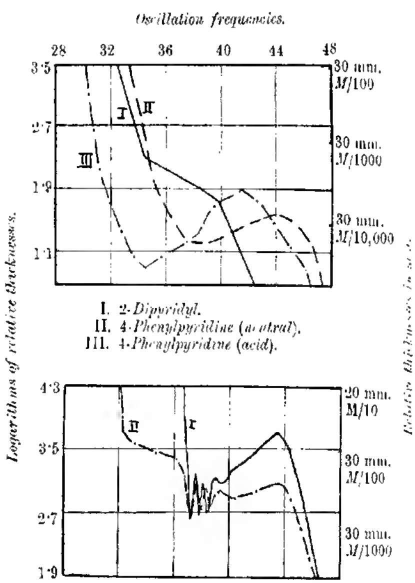
Solutions.

2-Dipyridyl, $C_{10}H_8N_2$.—The curve (Fig. 1, upper curves 1) shows that the pyridine band has almost disappeared, and there is

only a rapid extension of the transmitted rays between $1/\lambda$ 3450 and $1/\lambda$ 4000 (λ 2897—λ 2498). It may be mentioned that Hartley (*loc. cit.*) found a very weak band in dipyridyl between λ 2568 and λ 2310.

4-Phenylpyridine, $C_{11}H_9N$.—The curve (Fig. 1, upper curves II) shows a wide band, the head of which is at $1/\lambda$ 3900 (λ 2563). It is not unlike the solution band of pyridine (*loc. cit.*). There is no trace of the seven solution bands of benzene as described by

FIG. 1



I. 4-Phenylpiperidine (neutral).
II. 4-Phenylpiperidine (acid).

Hartley and Huntingdon (*Phil. Trans.*, 1879, **170**, i, 257), and by Baly and Collie (T., 1905, **87**, 1332). The large pyridine band covers the region of these seven bands, which extend between $1/\lambda$ 3690 (λ 2709) and $1/\lambda$ 4290 (λ 2330). The acid solution of the substance shows a marked change in the absorption; the band (Fig. 1, upper curves III) is shifted more towards the red end and is more persistent than that of the neutral solution. This result is similar to that observed by Baker and Baly and by the

with ... neutral and acid solutions of other pyridine compounds ... There is no appearance of the solution bands of benzene.

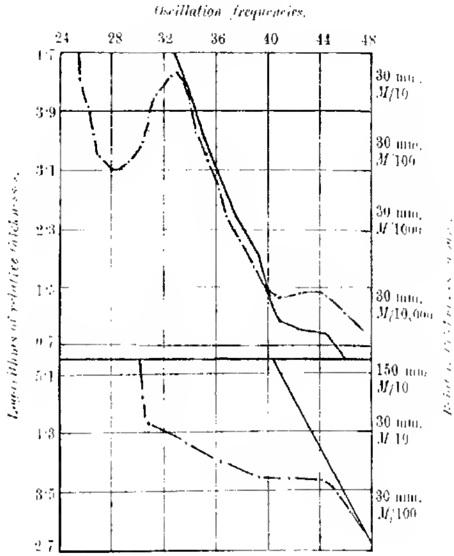
Piperidine, $C_5H_{11}N$.—Alcoholic solutions were first examined by Hartley (*loc. cit.*) and then by the author (*loc. cit.*), but no bands were observed in the ultra-violet regions. The author has studied slightly acid solutions, and compared these with equimolecular neutral solutions of the substance. The curves (Fig. 2, lower curves) show that in the acid solutions there is a rapid absorption of the rays as the thickness is increased between about $1/\lambda$ 3100 and $1/\lambda$ 4100 (λ 2720—λ 2240). This appears to indicate the presence of a very weak band, and it may be mentioned that the narrow vapour bands described by the author (*loc. cit.*) range between λ 2637 and λ 2438.

4-Phenylpiperidine, $C_{11}H_{15}N$.—The curve of the neutral solution (Fig. 1, lower curves I) is remarkable in that it exhibits four weak bands, which gradually disappear as the concentration is increased, and their place is taken by a single large band. These four bands are not unlike the benzene solution bands, but they are much weaker and closer together, and they differ also in position. The slightly acid solution (Fig. 1, lower curves II) shows striking changes. Three of the four weak bands become weaker, and they are shifted very slightly towards the more refrangible side. The most refrangible fourth band almost disappears, as well as the large band which appears at greater concentrations in the neutral solution. It is also to be noticed that the line of general absorption is shifted considerably towards the red end, and that the rapid extension of the transmitted rays between $1/\lambda$ 3300 and $1/\lambda$ 3600 (λ 3028 and λ 2776) may probably indicate the presence of a large weak band.

Nitrosopiperidine, $C_5H_{10}O_2N$.—The curve (Fig. 2, upper curve—dash and dot) shows a strong band, the head of which is at $1/\lambda$ 2850 (λ 3500), and probably connected with the nitroso-group and the colour of the substance. There is also a somewhat rapid extension of the transmitted rays between about $1/\lambda$ 3950 and $1/\lambda$ 4400 (λ 2530—λ 2270), beyond which the photographic plates are not susceptible. This may be the beginning of a large band which extends into the extreme ultra-violet regions. In any case, nitrosopiperidine differs from piperidine, for no solution band has been noticed in the latter compound (*loc. cit.*).

Benzoylpiperidine, $C_{12}H_{15}ON$.—The curve (Fig. 2, upper curve—continuous) shows no band, and in this respect it resembles the solution of piperidine. There may be traces of a rapid extension of the rays from about $1/\lambda$ 4150 (λ 2408) into the extreme ultra-violet regions, not unlike that in nitrosopiperidine.

FIG. 2.



Upper curves.

Benzoylpiperidine (continuous).
Nitrosopiperidine (dash and dot).

Lower curves.

Piperidine, neutral solution (continuous).
Piperidine, acid solution (dash and dot).

Piperazine, $C_4H_{10}N_2$.—Alcoholic solutions of various strengths were examined, but no bands were detected. The following numbers indicate the regions where general absorption begins:

		λ.
M/5·100 mm.	thickness general absorption begins at	2565
120	,, ,, ,, ,,	2575
140	,, ,, ,, ,,	2580
158	,, ,, ,, ,,	2590
M/10·10	,, ,, ,, ,,	2260
20	,, ,, ,, ,,	2320
30	,, ,, ,, ,,	2360
40	,, ,, ,, ,,	2430
60	,, ,, ,, ,,	2460
88	,, ,, ,, ,,	2540

The transparency of the solutions of piperazine and its compounds described below is very remarkable. In this direction it is comparable with neutral solutions of piperidine.

...hylpiperazine, $C_6H_{14}N_2$.—Alcoholic solutions of various strengths showed no band. The following numbers give the regions where general absorption begins in $M/100$-solutions:

					λ.
$M/100$-10 mm.	thickness	general	absorption	begins at	2200
30	,,	,,	,,	,,	2270
50	,,	,,	,,	,,	2300
70	,,	,,	,,	,,	2400
90	,,	,,	,,	,,	2420
120	,,	,,	,,	,,	2450
160	,,	,,	,,	,,	24[illegible]

...thylpiperazine, $C_6H_{14}N_2$.—No bands were observed in alcoholic solutions of various strengths, and the following numbers give the regions where general absorption begins in $M/10$-solutions:

					λ.
$M/10$-8 mm.	thickness	general	absorption	begins at	2300
16	,,	,,	,,	,,	2410
24	,,	,,	,,	,,	2480
40	,,	,,	,,	,,	2550
80	,,	,,	,,	,,	2600
120	,,	,,	,,	,,	2640
140	,,	,,	,,	,,	2800
156	,,	,,	,,	,,	2830

1 : 4-*Dibenzoyl-2-dimethylpiperazine*, $C_{20}H_{22}O_2N_2$.—This substance is not quite so soluble in alcohol as the 3-dimethyl compound. A saturated solution of about $M/140$-strength was investigated, but no bands were observed. The following numbers give the regions where general absorption begins:

					λ.
$M/140$-10 mm.	thickness	general	absorption	begins at	2800
20	,,	,,	,,	,,	2840
30	,,	,,	,,	,,	2870
$M/1400$-10	,,	,,	,,	,,	2570
20	,,	,,	,,	,,	2670
30	,,	,,	,,	,,	2730
$M/14,000$-10	,,	,,	,,	,,	2140
20	,,	,,	,,	,,	2270
30	,,	,,	,,	,,	2380

1 : 4-*Dibenzoyl-3-dimethylpiperazine*, $C_{20}H_{22}O_2N_2$.—No bands were observed in solutions of various strengths. The following numbers give the regions where general absorption begins:

					λ.
$M/100$-10 mm.	thickness	general	absorption	begins at	2780
20	,,	,,	,,	,,	2830
30	,,	,,	,,	,,	2850
90	,,	,,	,,	,,	2885
130	,,	,,	,,	,,	2930
$M/1000$-10	,,	,,	,,	,,	2590
20	,,	,,	,,	,,	2690
30	,,	,,	,,	,,	2730
$M/10,000$-10	,,	,,	,,	,,	2200
20	,,	,,	,,	,,	2400
30	,,	,,	,,	,,	2470

Vapours.

The vapours were examined in a 200 mm. tube at various temperatures and pressures, as described in the earlier investigation.

2-*Dipyridyl*, $C_{10}H_8N_2$.—At about 175° the rays were transmitted to λ 2144, and at about 185—190° to λ 2250, but they were slightly weak between λ 2660 and λ 2550. There was no appearance of any of the series of narrow bands found in pyridine vapour by the author (*loc. cit.*). The single weak band is comparable with the equally weak solution band.

4-*Phenylpyridine*, $C_{11}H_9N$.

$t°$.	Pressure in mm.	
80	890	The rays were transmitted to λ 2144.
85	896	,, ,, absorbed between λ 2540—λ 2350, and then feebly transmitted to λ 2270.
90	900	The rays were transmitted to λ 2600, beyond which there was complete absorption.

There was no appearance of any of the vapour bands of benzene and its homologues described by Hartley (*Phil. Trans.*, 1907, *A*, **208**, 475) or of pyridine vapour described by the author (*loc. cit.*). The single band is comparable with the solution band of pyridine, except in position.

3:5-*Dichloropyridine*, $C_5H_3Cl_2N$.—The following numbers give the wave-lengths, measured on the more refrangible edges, of the bands observed in the vapour.

Abbreviations: w = weak; v.w. = very weak; str. = strong; mod. str. = moderately strong; narr. = narrow.

30°. 814 mm. λ.	35°. 830 mm. λ.	30°. 814 mm. λ.	35°. 830 mm. λ.
2866 v.w.	2866 w.	2803 w., narr.	2805 w., wide
2863 ,,	2863 w.	2800 mod. str.	
2859 ,,		2795 w.	The rays were then fairly well absorbed to λ 2650 and then transmitted to λ 22[illegible].
2858 w.	2858 mod. str.	2790 mod. str.	
2852 mod. str.	2852 str.	2786 ,,	
2849 v.w., narr.	2849 v.w., narr.	2780 w.	
2845 mod. str.	2844 str.	2776 w.	
2843 ,,	2843 mod. str.	2764 w.	
2835 w.		2753 w.	14 bands and 1 large band.
2833 str.	2833 str., wide	2746 mod. str.	
2829 str.		2740 w.	
2827 w., narr.	2827 ,, ,,		
2823 ,, ,,		The rays were then feebly absorbed to about λ 2650, and then transmitted to λ 2200.	
2821 str.			
2820 w., narr.			
2818 str.	2819 ,, ,,		
2814 mod. str., narr.	2814 w., narr.		
	2812 mod. str.		
2811 mod. str.		30 bands and 1 large band.	
2806 w., narr.	2806 w., wide		

40°. 850 mm. λ.	80°. 910 mm. λ.	100°. 946 mm. λ.
2898 v.w.	B { 2912 v.w.	2940 w.
2895 w.	B { 2908 ,,	2928 v.w.
2879 v.w.	B { 2904 ,,	2926 ,,
2875 ,,	B { 2898 w.	The rays were then completely absorbed from λ 2920.
2869 ,,	B { 2895 mod. str.	
2864 w.	2890 v.w.	
2862 w.	The rays were then completely absorbed from λ 2885.	
2858 mod. str.		
2856 w., narr.		
2855 ,, ,,		
2850 mod. str.		
2845 w., narr.		
2843 ,, ,,		
2841 ,, ,,		
The rays were then absorbed to about λ 2540, and then transmitted to λ 2240. 14 bands and 1 large band.		

At the higher temperatures and pressures the bands became stronger and wider, and more hands appeared on the less refrangible side; and at the same time, the more refrangible bands gradually disappeared. Between the extreme temperatures of 30° and 100° the total number of narrow bands was forty-one, and there was a large band on the more refrangible side of these narrow bands, which is well marked at 35° and 45°.

On comparing the bands with those of pyridine (*loc. cit.*) there is no very close resemblance, and the former are weaker and shifted more towards the red end. The large band on the more refrangible side of the narrow hands is comparable with that of pyridine, except that it is also shifted more towards the red. The total number of bands found in the vapour of pyridine was forty-five, and one large band on the more refrangible side of the narrower bands.

2:3:5-*Trichloropyridine*, $C_5H_2Cl_3N$.—The absorption bands of the vapour of the substance were investigated in a tube 200 mm. long. Abbreviations as before (see p. 2290).

The bands do not appear to have a very close resemblance to those of pyridine. They are also much weaker, and shifted more towards the red end. There are two large groups, A′ and B′, and these are fairly comparable with the group A of 3:5-dichloropyridine. As in the other substances, at the higher temperatures and pressures, the narrower bands disappear, and a large band makes its appearance on the more refrangible side; this is particularly well shown at the temperatures of 60° and 75°. The

	20°. 759 mm. λ.	30°. 783 mm. λ.	45°. 829 mm. λ.	
			2916 v.w.	60°. 859 mm.
		2914 w.	2914 mod. str.	The rays were completely absorbed between λ 2940 — λ 28[illegible] and then transmitted to λ 22[illegible]
			2912 v.w.	
A	2910 v.w.	2911 mod. w.	2910 mod. str.	
		2909 w.	2909 ,,	
	2907 ,,	2906 mod. w.	2906 ,,	
	2903 ,,	2901 v.w.	2903 w.	
	2900 mod. w.	2900 mod. str.	2900 str.	
	2895 v.w.	2895 v.w.	2895 w.	
	2891 ,,	2891 ,,	2891 w.	75°. 889 mm.
	2888 ,,	2887 w.	2888 v.w.	The rays were absorbed between λ 2979 — λ 28[illegible] and then transmitted to λ 22[illegible]
	2883 ,,	2883 w.	2883 str.	
	2878 ,,	2876 w.	2876 mod. str.	
		2874 w.	2874 ,,	
B	2871 ,,	2869 w.	2870 w.	
		2863 w.	2863 w.	
	2858 ,,	2857 v.w.	2858 w.	
	2855 ,,	2853 w.	2853 w.	
	2848 mod. w.	2847 mod. str.	2846 mod. str.	
		2844 v.w.		
	The rays were then transmitted to λ 2140.	2812 mod. str.	The rays were then absorbed to λ 2750, whence they were transmitted to λ 2290.	90°. 920 mm. The rays were transmitted to λ 3000, beyond which there was complete absorption.
		The rays were then transmitted to λ 2140.		
	13 bands.	19 bands.	19 bands and 1 large band.	

fourteen narrower bands are fewer than those in the vapour of 3:5-dichloropyridine.

3:4:5-*Trichloropyridine*, $C_5H_2Cl_3N$.

t°.	Pressure in mm.	
60	860	The rays were feebly absorbed between λ 2840—λ 2710, and then transmitted to λ 2250.
75	890	The rays were absorbed between λ 2880—λ 2620, and then transmitted to λ 2280.
90	920	The rays were transmitted to λ 2920, and then there was complete absorption.

There was no appearance of any of the narrow bands observed in 2:3:5 trichloropyridine. The single large band is comparable with that found in the solution and in the solution of pyridine (*loc. cit.*). It is clear, therefore, that although the number of chlorine atoms is the same in both isomerides, their orientation determines the absorption to a very large extent.

2 : 3 : 4 : 5 *Tetrachloropyridine*, C_5HCl_4N.

	Pressure in mm.	
[illegible]	[illegible]	The rays were feebly absorbed between λ 2920—λ 2730, and then transmitted to λ 2300.
[illegible]	[illegible]	The rays were fairly well absorbed between λ 2940—λ 2700, and then transmitted to λ 2380.
	[illegible]	The rays were absorbed between λ 2970—λ 2670 and then transmitted to λ 2450.
	[illegible]	The rays were absorbed between λ 3000—λ 2600, and then feebly transmitted to λ 2560.

Again, therefore, there were no narrow bands found in the vapour of this compound, and the large band is comparable with that of the solution band (*loc. cit.*).

Tetrachloro-2-aminopyridine, $C_5H_2N_2Cl_4$.

	Pressure in mm.	
[illegible]	773	The rays were fairly well absorbed between λ 3000—λ 2800, and then transmitted to λ 2130.
[illegible]	773	The rays were absorbed between λ 3100—λ 2770, and then transmitted to λ 2500.
[illegible]	773	The rays were absorbed between λ 3200—λ 2740, and then transmitted to λ 2550.
[illegible]	773	The rays were transmitted to λ 3300, beyond which there was complete absorption.

Pentachloropyridine, C_5Cl_5N.

[illegible]	764	The rays were feebly absorbed between λ 2930—λ 2790, and then transmitted to 2250.
[illegible]	764	The rays were moderately well absorbed between λ 2980—λ 2780, and then transmitted to λ 2380.
[illegible]	764	The rays were almost completely absorbed between λ 3000—λ 2760, and then transmitted to λ 2450.
[illegible]	764	The rays were absorbed between λ 3010—λ 2740, and then transmitted to λ 2480.
[illegible]	764	The rays were absorbed between λ 3040—λ 2720, and then transmitted to λ 2480.
[illegible]	764	The rays were absorbed between λ 3080—λ 2650, and then transmitted to λ 2530.
[illegible]	764	The rays were completely absorbed from λ 3100.

All the narrow bands found in pyridine have completely disappeared, and a large band remained in each of these substances, comparable with the solution band of each (*loc. cit.*).

Methyl 2 : 3 : 4-*Trichloropicolinote*, $C_7H_4O_2NCl_3$

	Pressure in mm.	
[illegible]	760	The rays were very weakly absorbed between λ 2900—λ 2750, and then transmitted to λ 2260.
[illegible]	760	The rays were fairly well absorbed between λ 2990—λ 2700, and then transmitted to λ 2420.
[illegible]	760	The rays were almost completely absorbed between λ 3010—λ 2670, and then transmitted to λ 2470.
[illegible]	760	The rays were completely absorbed between λ 3050—λ 2620 and then transmitted to λ 2530.
[illegible]	760	The rays were completely absorbed from λ 3070.

2 : 3 : 4-*Trichloropicolinamide*, $C_6H_3ON_2Cl_3$.

190	770	The rays were moderately well absorbed between λ 3200—λ 2900, and then transmitted to λ 2150.
200	770	The rays were well absorbed between λ 3250—λ 2800, and then transmitted to λ 2530.

2 : 3 : 4-*Hexachloropicoline*, C_6HNCl_6.

130	770	The rays were well absorbed between λ 2940—λ 2630, and then transmitted to λ 2540.
140	770	The rays were transmitted to λ 2960, beyond which there was complete absorption, except that the Cd line 2573 was visible.
150	770	There was complete absorption of the rays from λ 2980.

So that in all these three substances there was no appearance of any narrow bands, and the large band of each is comparable with the solution band found previously (*loc. cit.*).

4-*Phenylpiperidine*, $C_{11}H_{15}N$.

t°.	Pressure in mm.	
80	760	The rays were transmitted to λ 2190.
90	760	,, ,, ,, λ 2230, but there was a distinct weakening between λ 2470—λ 2330.
100	760	The rays were well absorbed from λ 2550 to the series of Cd lines λ 2329—λ 2265 which were just visible.
110	760	The rays were absorbed from λ 2650.
120	760	,, ,, ,, ,, λ 2700.

That is to say, there are no series of bands like those found either in the vapour of benzene and its homologues by Hartley, nor like those found in piperidine by the author (*loc. cit.*). There are merely strong indications of a band comparable with the large solution band found in the greater thicknesses, and there is no appearance of the four very weak bands found in the more dilute solutions.

In connexion herewith the author has examined very thin films of the substance in the manner described in previous communications to see whether such films absorbed the light like the solution. Four very weak bands were found which are comparable with the solution bands; but, as in previous comparisons also, they are shifted slightly more towards the red end. The heads of these four weak bands are at about λ 2697, λ 2665, λ 2627, λ 2556; or, in oscillation frequencies, at 1/λ 2706, 1/λ 3750, 1/λ 3805, 1/λ 3911.

Nitrosopiperidine, $C_5H_{10}ON_2$.

t.	Pressure in mm.	
[illegible]	752	The rays were transmitted to λ 2144.
[illegible]	822	,, ,, ,, ,, λ 2500, but the two Cd lines 2194 and 2144 were just visible.
[illegible]	852	The rays were transmitted to λ 2650.
[illegible]	882	,, ,, ,, ,, λ 2750.
[illegible]	928	The rays were moderately well absorbed between λ 3800—λ 3450, and then transmitted to λ 2850.

The observations, therefore, prove that all the thirty-seven vapour bands of piperidine vapour described by the author (*loc. cit.*) have completely disappeared. The single band extending into the visible regions, like that of the solution band, is connected with the nitroso-group, and therefore with the colour of the compound. It shows no signs of being resolved into a series of narrow bands.

Benzoylpiperidine, $C_{12}H_{15}ON$.

t.	Pressure in mm.	
100	765	The rays were transmitted to λ 2190.
120	765	,, ,, ,, ,, λ 2270.
150	765	,, ,, ,, ,, λ 2580.
170	765	,, ,, ,, ,, λ 2680.
190	765	,, ,, ,, ,, λ 2750.

So that, like the vapour of nitrosopiperidine, all the vapour bands of piperidine have disappeared, and no other band was observed.

Piperine, $C_5H_{10}N{\cdot}C_{12}H_9O_3$.—The vapour was examined at various temperatures. At about 165° there appeared a large band between λ 3250 and λ 2830; and there was no trace of any of the narrower bands found in the vapour of piperidine. With regard to the solutions, Hartley (*Phil. Trans.*, 1885, **176**, 471) found a wide band between λ 360 and λ 270, and Dobbie and Fox (T., 1912, **103**, 1193) confirmed this. The latter observers also showed that this band was similar to that of piperic acid, and they draw the conclusion that substances the molecules of which are composed of two nuclei will give the characteristic band of the unsaturated one. The author discusses this remark later.

Piperazine, $C_4H_{10}N_2$.

t.	Pressure in mm.	
100	765	The rays were transmitted to λ 2144.
120	765	,, ,, ,, λ 2400.
130	765	,, ,, ,, λ 2550.
160	765	There were three weak somewhat diffuse bands at λ 2703, λ 2700, and λ 2696, and the rays were then transmitted to λ 2580.
175	765	These three weak bands became a little stronger and the measurements are λ 2704, λ 2700, and λ 2698. The rays were then transmitted to λ 2625.

The three vapour bands were well marked, and the middle one stronger than the other two.

2-Dimethylpiperazine, $C_6H_{14}N_2$.

t°.	Pressure in mm.	
145	765	There were three diffuse bands at λ 2695—λ 2690, λ 2638—λ 2635, λ 2584—λ 2581, and the rays were then transmitted to λ 2490. The distance between the separate bands is about 55 units.
155	765	There were two bands at λ 2695—λ 2690 and λ 2638—λ 2635, and the rays were then transmitted to λ 2590.

3-Dimethylpiperazine, $C_6H_{14}N_2$.

t°.	Pressure in mm.	
130	765	There were three diffuse bands at λ 2748, λ 2688—λ 2684, λ 2634—λ 2630, and the rays were then transmitted to λ 2535.
140	765	There were three bands at λ 2741—λ 2739, λ 2690—λ 2685, λ 2634—λ 2630, and the rays were then transmitted to λ 2580. The distance between the separate bands is about 55 units.
150	765	The rays were absorbed between λ 2745—λ 2739, and λ 2688—2683, and then transmitted to λ 2660.

Each of the vapours of the two isomerides showed, therefore, three diffuse bands which are sharper on the more refrangible edges. They are also considerably wider apart than the vapour bands of piperazine, and the bands of the 3-compound are shifted more towards the red end than the corresponding ones of the 2-compound by about 50 units. The instability of the dibenzoyl derivatives made it difficult to take exact observations of the absorption of their vapours, but at the lower temperatures of observation no bands corresponding with the piperazine bands were observed. In the case of 1:4-dibenzoyl-3-dimethylpiperazine (m. p. 153°) at 170° the rays were transmitted to λ 2200. At 190° they were transmitted to λ 2270. In connexion with piperazine and its compounds it is of some interest to recall that the author (T., 1910, **97**, 1648) found four weak bands in the vapour of pyrrole, whereas neither solutions nor thin films of the substance exhibited any bands.

General Results.

The results of the preceding observations show that solutions of 2-dipyridyl possess a weak pyridine band, whereas 4-phenylpyridine has a strong one; that neutral solutions of piperidine show no bands, whereas acid solutions show a weak potential band, which covers the region of the vapour bands of piperidine described by the author (*loc. cit.*); that neutral solutions of 4-phenylpiperidine possess four weak bands, probably the residues of four benzene

[illegible] bands, whereas acid solutions exhibit these four bands [illegible]ebly, and they also show strong indications of a weak [illegible] band on the less refrangible side; that neutral solutions [illegible]ylpiperidine have no bands, whereas nitrosopiperidine has [illegible] band, most likely connected with the nitroso-group; that piperazine and its derivatives have no bands, and are very transparent even in the strongest solutions.

As regards the vapours, those of 2-dipyridyl and 4-phenylpyridine show bands comparable with the solution bands. On the other hand, the vapours of 3:5-dichloropyridine and 2:3:5-trichloropyridine have a considerable number of narrow bands on the less refrangible edge of the pyridine band, and these narrow bands are completely absent from the solutions (*loc. cit.*). Also the vapours of 3:4:5-trichloropyridine, and the other pyridine derivatives investigated before, show no narrow bands, but only bands which are comparable with the strong solution bands (*loc. cit.*). Furthermore, the vapours of 4-phenylpiperidine, nitrosopiperidine, and benzoylpiperidine show none of the characteristic vapour bands of either piperidine or benzene. The vapour of piperine has one large band comparable with the solution band; the piperazine and its derivatives show three weak bands each. The latter are also interesting by reason of their great transparency; and, in this respect, they are like solutions of piperidine and pyrrole (*loc. cit.*).

An increase in the number of chlorine atoms in the pyridine nucleus is accompanied by a decrease in the number of narrow vapour bands, but the spatial position of the atoms is also a factor; for, although 2:3:5-trichloropyridine vapour exhibits a considerable number of such bands, the isomeric 3:4:5-trichloropyridine vapour has none. Similar results have been found by the author in the chloro- and bromo-derivatives of benzene and toluene (T., 1911, **99**, 811, 1699). This destruction of the narrow bands also occurs in the duplicated molecule 2-dipyridyl; and the author has shown that the vapour of naphthalene, a condensed benzene molecule, and the vapour of quinoline, a condensed benzene and pyridine molecule, show none of the narrow bands found in the vapours of benzene and pyridine (T., 1910, **97**, 1035; 1912, **101**, 1315).

With regard to 4-phenylpiperidine, the appearance of the four weak benzene bands in neutral solution, and of an additional weak pyridine band in the acid solution, together with the absence of the four bands in 4-phenylpyridine, would seem to lend some support to the conclusion of Dobbie and Fox (*loc. cit.*) that substances the molecules of which are composed of two nuclei will give the characteristic bands of the unsaturated one. This is only

partly true, even on the assumption that the four weak solution bands of 4-phenylpiperidine are the residues of the well-known seven solution bands of benzene. It is not true at all of the vapours of the substance, for not one of the numerous vapour bands of benzene or pyridine were observed.

That the varying valency of the nitrogen atom is of fundamental importance follows from the fact that the acid solutions of piperidine and 4-phenylpiperidine show indications of the large pyridine band which are absent from the neutral solution; but investigations with the isomerides of 4-phenylpyridine and 4-phenylpiperidine are necessary before a full discussion can be submitted.

It is established from these and earlier investigations that where a vibrating vapour molecule exhibits a series of narrow bands, such bands wholly disappear when the substance is in solution, and the solvent must therefore exercise an outstanding influence. The author has suggested before that the radiant energy of the source of light acting on the various atoms and groups of atoms in a molecule initiates the vibrations which produce selective absorption, and that the interactions of the different oscillatory centres, which may be centres of electronic vibrations, are modified by the type of nucleus as in benzene and pyridine; by the type and number of the side-chains as in the various derivatives of benzene and pyridine; by their physical condition as in the vapours at different temperatures and pressures; and by the solvent which absorbs a part of the radiant energy, whereby new interacting centres of oscillation are set in motion, and compensating effects take place, and damping and resisting forces brought into action.

I desire to thank the Government Grant Committee of the Royal Society, by whose assistance a part of the cost of the research was defrayed; Professor Pope for the piperazine compounds; and Dr. Sell for the pyridine compounds, with the exception of 4-phenylpyridine and 4-phenylpiperidine, for which I am indebted to Dr. Mills.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

INDEX OF AUTHORS' NAMES.

TRANSACTIONS AND PROCEEDINGS. 1913.

(Marked T. and P. respectively.)

D.

E.

F.

G.

N.

P.

U.

V.

W.

Y.

INDEX OF SUBJECTS.

TRANSACTIONS AND PROCEEDINGS. 1913.

(Marked T. and P. respectively.)

Single organic compounds of known empirical formula will be found in the Formula Index, p. 2323.

A.

B.

C.

H.

I.

K.

L.

FORMULA INDEX.

The following index of organic compounds of known empirical formula is arranged according to Richter's system (see *Lexikon der Kohlenstoff-Verbindungen*).

The elements are given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

The compounds are arranged—

Firstly, in groups according to the number of carbon atoms (thus C_1 group, C_2 group, etc.).

Secondly, according to the number of other elements besides carbon contained in the molecule (thus 5 IV indicates that the molecule contains five carbon atoms and four other elements).

Thirdly, according to the nature of the elements present in the molecule (given in the above order).

Fourthly, according to the number of atoms of each single element (except carbon) present in the molecule.

Salts are placed with the compounds from which they are derived. The chlorides, bromides, iodides, and cyanides of quaternary ammonium bases, however, are registered as group-substances.

C_1 Group.

1 II

1 III

C_2 Group.

2 III

2 IV

C_3 Group.

4 IV

C_5 Group.

5 III

5 IV

C_6 Group.

6 II

6 III

C_7 Group.

7 III

8 III

8 IV

8 V

C_9 Group.

9 II

9 III

9 IV

C_{10} Group.

10 II

10 III

10 IV

C_{11} Group.

11 III

11 IV

C_{12} Group.

12 II

12 IV

C_{13} Group.

13 III

13 IV

13 V

C_{14} Group.

14 IV

C_{15} Group.

15 II

15 III

15 IV

15 V

C_{16} Group.

16 III

C_{17} Group.

17 IV

C_{18} Group.

18 IV

18 V

C_{19} Group.

19 III

C_{20} Group.

20 III

20 IV

C_{21} Group.

21 III

C_{23} Group.

C_{24} Group.

24 IV

C_{25} Group.

25 III

C_{26} Group.

26 IV

C_{27} Group.

C_{31} Group.

31 III

31 IV

C_{32} Group.

32 IV

C_{33} Group.

C_{34} Group.

34 III

C_{35} Group.

C_{48} Group.

C_{50} Group.

C_{52} Group.

C_{54} Group.

C_{56} Group.

C_{58} Group.

C_{61} Group.

C_{66} Group.

C_{68} Group.

C_{70} Group.

C_{71} Group.

C_{84} Group.

C_{86} Group.

ERRATA.

Vol. CIII. (Trans., 1913).

Page	Line	
153	27	*for* "ethyl di-*p*-toluoyl-" *read* "ethyl di-*p*-nitrobenzoyl-."
165	1	asterisk refers to footnote on p. 164.
611	16-17	*for* "whence $[\alpha]_D + 7{\cdot}21°$ and $[M]_D + 22{\cdot}9°$" *read* "whence $[\alpha]_D + 3{\cdot}72°$ and $[M]_D + 11{\cdot}8°$."
	Fig.	
638	1	Ordinates: *for* "1·200" and "1·400" *read* "1·02" and "1·04" (upper curve should accordingly be much steeper).
947		in formula II *for* "CH ⁄ \ CH_2 ⋮" *read* "CH_2 ⁄ \ CH_2 |".
	Line	
1565	19	*for* "bromobenzene" *read* "bromonaphthalene."
1571	20	,, "derived" *read* "derivative."
1582	5	,, "$C_{14}H_{14}O_{12}Ba_3$" *read* "$C_{14}H_{14}O_{12}Ba_3,4H_2O$."
1588	7* and 26*	in equation *omit* "+ H_2O."
1613	16*	*for* "$C_6H_5{\cdot}C \vdots N{\cdot}OH$" *read* "$C_6H_5{\cdot}CH \| N{\cdot}OH$"
1624	6	,, "tube to 100°" ,, "tube with benzene to 100°."
1852	13	,, "$C_{15}H_9O_3N_2$" ,, "$C_{15}H_8O_3N_2Na$."
1928	1*	,, "marked" ,, "masked."
2301	2*	,, "**Willsdon**" ,, "**Willson.**"
2311	29*	

* From bottom.

Organic Chemistry.

Preparation of Hydrocarbons with Two Conjugated Double Linkings. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. [illegible]642).—When $\alpha\gamma$-glycols of the general formula

RRC(OH)·CHR·CR(OH)·CHRR

(where R is an alkyl group or hydrogen) are heated with agents that withdraw water, they furnish compounds of the general formula

RRC:CR·CR:CRR.

Butane-$\alpha\gamma$-diol when heated with 30% sulphuric acid at 170—180° yields a 10% yield of erythrene; with phosphoric acid at 300° the yield is 60%, and with magnesium sulphate at 300—400° about 50%, whilst β-methylbutane-$\beta\delta$-diol with potassium hydrogen sulphate at [illegible]—170° gives rise to a 20% yield of isoprene.

$\alpha\alpha$-*Dimethylerythrene*, b. p. 74°, is obtained in 40% yield from δ-methylpentane-$\beta\delta$-diol at 160° with aluminium chloride.

F. M. G. M.

Diisobutenyl from Tribromoisobutane. VL. KRESTINSKI and K. KRIVOROTKO (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 946—949).—The action of magnesium on $\alpha\beta\gamma$-tribromoisobutane, $CH_2Br{\cdot}CMeBr{\cdot}CH_2Br$ (compare Pogorshelski, A., 1905, i, 315), in presence of ether and treatment of the product obtained with water, yields, as principal product, $\beta\epsilon$-dimethyl-$\Delta^{\alpha\epsilon}$-hexadiene, $CH_2{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH_2$, D 0·7512, n_D 1·4309 (compare Pogorshelski, A., 1899, i, 785). Treatment of the latter with hydrogen bromide yields the $\beta\epsilon$-dibromo-$\beta\epsilon$-dimethylhexane, $CMe_2Br{\cdot}CH_2{\cdot}CH_2{\cdot}CMe_2Br$, m. p. 68°. T. H. P.

Preparation of Halogen Derivatives of the Paraffin Series. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 261677, 263716).—A satisfactory yield of chlorinated or brominated hydrocarbons is obtained by mixing the parent hydrocarbons in a gaseous condition with the vapour of the required halogen. Mixtures of chloro- and dichloro-, and of bromo- and dibromo-hexane were thus obtained; chloroisopentane furnished $\alpha\beta$-dichloro-β-methylbutane, whilst chloropentane gave rise to a *dichloropentane*, b. p. 130—150°. In the second patent it is shown that the halogenation can be effected by means of the silent electric discharge; thus n-pentane furnishes a mixture of α- and γ-chloropentane. F. M. G. M.

Addition of Bromine to Chlorinated Olefines. WALTHER HERZ and W. RATHMANN (*Ber.*, 1913, **46**, 2588—2590. Compare this vol., ii, [illegible] 765).—The reactions between bromine and di-, tri-, and tetrachloroethylene have been studied. Known quantities of the two substances, with or without diluents, were sealed up in test-tubes of dark brown glass, and kept at 25° for different intervals, when the tubes were broken under potassium iodide and the unabsorbed bromine

titrated. By employing a large excess of hydrocarbon the reaction could be expressed in the form, $1/t \log a/(a-x)$, where a is the initial concentration of bromine and x the amount absorbed after the time t.

cis-Dichloroethylene was found to absorb bromine nearly twice as fast as the *trans*-modification. No constant values could be obtained in the case of trichloroethylene, but *aaβ-trichloro-aβ-dibromoethane* was isolated as a pale yellow, pungent smelling liquid, b. p. 126°/85 mm. The influence of diluents was studied in the case of tetrachloroethylene.

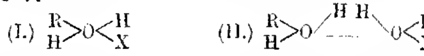
J. C. W.

The Action of Sodium Ethoxide on Tetranitromethane. A Caution. Alexander K. Macbeth (*Ber.*, 1913, **46**, 2537—253?; *Chem. World*, 1913, **2**, 328).—The addition of sodium ethoxide to tetranitromethane may give rise to serious explosions.

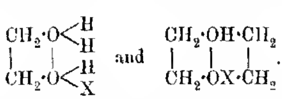
In an experiment in which 30 grams of tetranitromethane were being treated with an alcoholic solution of sodium ethoxide, the formation and separation of the sodium derivative of trinitromethane appeared to be proceeding in a normal manner when a violent explosion occurred doing serious damage to the experimenter and to the laboratory.

D. F. T.

Mechanism of the Reactions between Alcohols and Mineral Acids. Oxonium Compounds of Hydrogen Haloids. Alexei E. Favorski (*J. pr. Chem.*, 1913, [ii], **88**, 480—495. Compare McIntosh, T., 1904, **85**, 919; 1905, **87**, 784; A., 1905, i, 254, 677; 1906, i, 481, and Mokievski, A., 1899, i, 729).—Di*iso*propylcarbinol, ethyl*tert.*-butylcarbinol, and *iso*propyl*tert.*-butylcarbinol (this vol., i, 12), readily form with hydrogen haloids, crystalline oxonium salts of the following types:



The compounds of the second type are the more stable, and are obtained by the action of the hydrogen haloid on the alcohols at 0° or the ordinary temperature; at lower temperatures compounds of the first type are produced. The oxonium compounds derived from glycols (Mokievski, *loc. cit.*) and diethylene ether are formulated as follows:



The author considers that the intermediate formation of oxonium compounds of this kind must be taken into account in explaining the mechanism of all reactions in which alcohol and mineral acids simultaneously take part, and illustrates his views by reference to the formation of ethers and hydrocarbons by the action of acids on alcohols, and the transformation of glycols into ketones and aldehydes under the influence of acids.

[With Anna I. Umnova.]—The *compounds* of di*iso*propylcarbinol with hydrogen iodide and hydrogen bromide, $2C_7H_{15}\cdot OH,HX$,

separate in colourless crystals, m. p. 77—78° and 68—69° respectively, by passing the hydrogen haloids into the carbinol at the ordinary temperature; the corresponding *hydrochloride* is very hydroscopic.

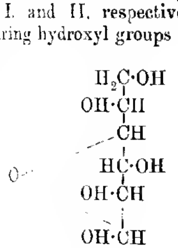
[With P. Aschmarin.]—The following *compounds* of ethyl *tert.*-butylcarbinol are described: $2C_7H_{15}\cdot OH,HI$, m. p. 74—76°; $2C_7H_{15}\cdot OH,HBr$, m. p. 52—54°; $C_7H_{15}\cdot OH,HBr$, m. p. 13—17°; $C_7H_{15}\cdot OH,HCl$, m. p. 23—25°; $2C_7H_{15}\cdot OH,HCl$.

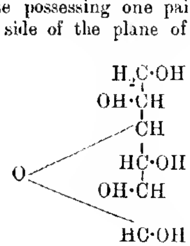
[With Ernst Fritzmann.]—The compounds of *iso*propyl*tert.*-butylcarbinol with hydrogen iodide, $2C_8H_{17}\cdot OH,HI$, and hydrogen bromide, $2C_8H_{17}\cdot OH,HBr$, have m. p. 78—80° and 77—78° respectively.

F. B.

The Spacial Arrangement of the Hydroxyl Groups of Polyhydroxy-compounds. The Configuration of the Saturated Glycols and of α- and β-Dextrose. Jacob Böeseken (*Ber.*, 1913, 46, 2612—2627).—The influence of hydroxy-compounds on the conductivity of boric acid solutions is set forth in a series of experiments, most of which have already been described (this vol., ii, 347; i, 742). The main conclusion arrived at by the author, that exaltation of the conductivity is caused by those compounds in which two hydroxyl groups attached to neighbouring carbon atoms are also in the same plane, thus permitting the formation of ring combinations with the boric acid, is further exemplified and extended to the determination of the configuration of saturated glycols and of α- and β-dextrose. Saturated glycols have no positive influence, and therefore the hydroxyl groups are arranged on opposite sides of the neighbouring carbon atoms. Alcohols with more than two hydroxyl groups are likely to have some pair or other in the favourable position, and glycerol, erythritol, β-nitro-αγδ-trihydroxy*iso*butane, pentaerythritol, mannitol, dulcitol, and sorbitol have positive influences in increasing degrees.

α- and β-Methylglucosides, sucrose, and raffinose have no pair of hydroxyl groups in the favourable position, and have only a minimal, negative influence on boric acid. α-Dextrose has a greater influence than β-dextrose, and the sugars are therefore represented by the formulæ I. and II. respectively, α-dextrose possessing one pair of neighbouring hydroxyl groups on the same side of the plane of the ring.

(I.) 

(II.) 

The gradual fall in the conductivity of α-dextrose–boric acid and the rise in conductivity of β-dextrose–boric acid coincide with the mutarotation, and the constants for the mutarotation and the alteration in

conductivity are equal. If the mutarotation were accompanied by the opening of the ring, a chain of five labile hydroxyl groups would be formed, and the conductivity of the boric acid solution would be increased. The fact that this does not happen supports E. F. Armstrong's view that mutarotation takes place without disturbing the γ-oxide ring (T., 1903, **83**, 1305). J. C. W.

Conversion of Cellulose into Dextrose. HERMANN OST (*Ber.*, 1913, **46**, 2995—2998).—In reply to the interpretation placed by Willstätter and Zechmeister (this vol., i, 955) on the optical activity of the dextrose obtained by Ost and Wilkening (A., 1910, i, 364) from the hydrolysis of starch by sulphuric acid, the author maintains that the other experiments of the latter investigators supply final evidence that the yield of dextrose was in reality over 90% of the starch used, and attributes the low optical activity to the well known considerable effect of the presence of traces of impurity. D. F. T.

Electrical Conductivity of Some Platinum Compounds of Organic Disulphides. LEO A. TSCHUGAEV and A. KOBLJANSKI (*Zeitsch. anorg. Chem.*, 1913, **83**, 8—26).—In order to avoid the complications introduced by water, the author has examined the conductivity of a large number of complex compounds in methyl alcohol. It is found that compounds of the type $[PtS''Cl_2]$, where S'' is a dithioether, are non-conducting, but that further addition of disulphide causes a rapid increase of conductivity. An equilibrium occurs: $[PtS''Cl_2] + S'' \rightleftarrows [Pt2S'']Cl_2$, the latter compound then becoming ionised.

The compounds of ethylene-dithioglycol ethers have been compared with those from propylene-dithioglycol ethers. The platinum chloride compound of the *diethyl ether*, $[PtCl_2,C_3H_6(SEt)_2]$, crystallises in needles, m. p. 135°, and the *di*-n-*propyl ether* compound has m. p. 133°. It has not been found possible to prepare sufficiently pure compounds from $\alpha\alpha$- and $\alpha\epsilon$-dithioglycol ethers, but the conductivity of mixed solutions of these sulphides with stable $\alpha\beta$-compounds has been determined. The $\alpha\alpha$-dithio-ethers have the least tendency to form complexes.

The conclusions are in accordance with Werner's co-ordination theory. C. H. D.

Compounds of Platinous Nitrite with Organic Dithio-ethers. LEO A. TSCHUGAEV and WITALIUS G. CHLOPIN (*Zeitsch. anorg. Chem.*, 1913, **82**, 401—419. Compare A., 1910, i, 354; 1912, i, 70).—Like the halogen compounds, platinous nitrite readily forms isomeric compounds with dithio-ethers. The bimolecular compound is the first product, and is more stable than in the case of the halogen compounds, so that the conversion into the unimolecular form takes place much less readily. The latter modifications are most readily obtained from the chlorides and soluble nitrites.

Diethyl ethylene dithioether and platinous nitrite form a *compound*, $[Pt2C_2H_4(SEt)_2]Pt(NO_2)_4$, m. p. 170—170·5°. It reacts with Reiset's chloride to form the yellow compound $[Pt4NH_3]Pt(NO_2)_4$. The former

compound is also obtained from the bimolecular chloride and sodium nitrite. The unimolecular *compound*, $C_2H_4(SEt)_2,Pt(NO_2)_2$, has m. p. 161—161·5°, and does not react with Reiset's chloride. Excess of the ether, together with potassium platinonitrite, convert it into the bimolecular modification.

Dimethyl ethylene dithioether and platinous nitrite yield the bimolecular *compound*, $[Pt2C_2H_4(SMe)_2]Pt(NO_2)_4$, m. p. 214·5—215°, which is slowly converted, even in the cold, into the unimolecular compound, m. p. 210·5—211°, by an excess of the ether.

The dipropyl dithioether also yields two *compounds*, m. p. 184·5—185° and 179—179·5° respectively, and the *compounds* from the di-*n*-butyl dithioether have m. p. 181—181·5° and 172—172·5° respectively.

Diethyl propylene dithioether yields a *compound* with m.p. 229—229·5°, the constitution of which is uncertain.

Diethyl β-hydroxypropylene αγ-dithioether yields a sparingly soluble *compound*, m. p. 182—182·5° (decomp.), and probably bimolecular.

Dimethyl sulphide yields only a unimolecular compound with platinous nitrite, all attempts to prepare a bimolecular modification having failed. C. H. D.

Complex Compounds of Organic Sulphides with Quadrivalent Platinum. Leo A. Tschugaev and J. Benevolenski (*Zeitsch. anorg. Chem.*, 1913, **82**, 420—425).—Isomerism has not hitherto been observed in compounds of quadrivalent platinum with organic sulphides. It is now found that compounds with two complex ions are obtained from hydrogen platinichloride and sulphides, but that their composition does not correspond with the expected formulæ

Methyl sulphide and platinic chloride yield a precipitate with the empirical composition $Pt,2Me_2SCl_3$, which at 110—115° suddenly changes from red to yellow, yielding a mixture of two substances, which may be separated by means of chloroform. The less soluble compound, $PtCl_4,2Me_2S$, darkens from 150°, whilst the other,

$$PtCl_2,2Me_2S,$$

has m. p. 157°. The original compound is thus $[Pt,4Me_2S]PtCl_6$. A similar compound is obtained from diethyl ethylene dithioether. C. H. D.

Formic Acid as a Solvent. Ossian Aschan (*Chem. Zeit.*, 1913, 37, 1117—1118).—The solubilities of a number of inorganic salts and organic compounds in 95% formic acid are given. A wide range of metallic salts is found to dissolve in this acid, but not so freely as in water. Easily reduced salts are liable to decomposition, but, whereas iodine is liberated from sodium iodide in the cold, potassium iodide is stable. The acid decomposes pinene nitrosochloride and the salts of weak organic acids, and esterifies certain alcohols, such as borneol. With these exceptions, it is a useful solvent for many organic compounds, including in addition to bromo-carboxylic acids, for which it has already received frequent application, polycyclic hydrocarbons, terephthalic acid, uric acid, indigotin, and alizarin.

The acid is easily volatilised on the water-bath, and deposits large

crystals of many substances, as, for example, suberic acid, citric acid, α-bromocamphor, α-nitronaphthalene, and *m*-dinitrobenzene. It is now cheaper than glacial acetic acid, and usually exhibits a greater difference of solvent power between the hot and cold liquid, and, in spite of its blistering effect, it is deserving of more extensive application. J. C. W.

Displacement of Acetic Acid from Solutions of its Salts by Carbon Dioxide Under High Pressure. VLADIMIR N. IPATIEV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 992—994. Compare Ipatiev and Verchovski, A., 1909, ii, 564; 1911, ii, 716).—The author has investigated the action of carbon dioxide under a pressure of 50 atmospheres on aqueous solutions of various acetates, both at the ordinary temperature and at 90°. With 12% calcium acetate solution, crystalline calcium carbonate was precipitated in some cases, but not in others; in one instance, 1 gram of the carbonate was obtained from 50 c.c. of the acetate solution after seven days at 90°. In a similar manner barium acetate yields the carbonate, and copper acetate the basic carbonate, $CuCO_3,Cu(OH)_2,H_2O$, but no precipitate was obtained from nickel acetate, even after several months. T. H. P.

The Action of Acetic Anhydride on Ferric and Chromic Nitrates. RUDOLF F. WEINLAND and HANS REIHLEN (*Zeitsch. anorg. Chem.*, 1913, **82**, 426—430).—The compounds described by Späth (A., 1912, i, 408) as normal ferric and chromic acetates are really acetates of the triferri-(chromi)hexa-acetate-base, and the method of preparation has no advantage over those usually adopted. Both compounds yield the characteristic platinichlorides. C. H. D.

Production of Hydrocarbons from a Solution of Sodium Stearate by Electrolysis. H. T. F. RHODES (*Chem. News*, 1913, **108**, 201).—The production of hydrocarbons by the electrolysis of aqueous solutions of the salts of aliphatic acids increases in difficulty with increasing molecular weight of the acid, probably owing to the partial hydrolysis which occurs when the salts are dissolved in water. By employing a small current, however, the author has succeeded in electrolysing an aqueous solution of sodium stearate which had been acidified with acetic acid, and has obtained a hydrocarbon very similar in physical properties to paraffin wax. The substance could only be detected after the solutions had been preserved for some time, and could not be identified owing to the small yield. H. W.

Oxidising Action of Potassium Permanganate in an Alkaline Medium on Normal, Saturated Fatty Acids. EVGENII S. PRSHEVALSKI (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 891—905; *J. pr. Chem.*, 1913, [ii], **88**, 495—501. Compare A., 1911, i, 947).—The action of faintly alkaline potassium permanganate solution on various acids of the aliphatic series has been investigated.

With 1% permanganate solution, *n*-heptoic acid gives (1) valeric, butyric, and propionic acids; (2) a ketonic acid, probably

$$CH_3\cdot[CH_2]_4\cdot CO\cdot CO_2H,$$

m. p. 51—52°; (3) a dibasic dihydroxy-acid, $C_5H_8(OH)_2(CO_2H)_2$, and (4) adipic, glutaric, succinic, and oxalic acids. Under similar conditions, *n*-hexoic acid yields glutaric acid, in addition to the acids already mentioned (*loc. cit.*). *n*-Valeric acid gives butyric, propionic, oxalic, and succinic acids. At either 37—38° or 100°, *n*-butyric acid yields oxalic and propionic acids, whilst if 5% permanganate is used, β-hydroxybutyric and *iso*malic acids are also formed. Propionic acid gives carbon dioxide and oxalic acid, and if the oxidation is carried out in a solution containing 5% of alkaline hydroxide, hydroxypropionic acid.

The results obtained show that the difficulty of oxidising normal fatty acids increases with the shortness of the carbon-atom chain (compare Margulies, A., 1894, i, 491), and that the products obtained vary with the conditions of oxidation. In every case oxidation takes place at two points of the carbon-atom chain: (1) at the carbon atom adjacent to the carboxyl group, the next lower fatty acid being formed, and (2) at the carbon atom next to the methyl group.

Since the dibasic acids obtained never contained the same numbers of carbon atoms as the original acids, but always one less, the methyl group must undergo oxidation to carboxyl and then to carbon dioxide.

That oxidation of two carbon atoms simultaneously in one molecule of an acid may take place is shown by the formation of a dihydroxy-dicarboxylic acid from *n*-heptoic acid. As intermediate products of these oxidations, hydroxy- and keto-acids are formed.

In view of the ready oxidisability of the methyl group, which is adjacent to a partly oxidised carbon atom, the possibility of the formation of acetic acid in these oxidations seems doubtful.

With *n*-butyric acid, oxidation is accompanied by isomerisation of the normal propyl group to the iso-group. T. H. P.

Lignoceric Acid. HANS MEYER, LEO BROD, and WALTHER SOYKA (*Monatsh.*, 1913, **34**, 1113—1142).—Lignoceric acid is shown to occur in the "solid paraffin" fraction of tar distilled from Bohemian lignite. With a view to ascertaining whether lignoceric acid, $C_{24}H_{48}O_2$, has the normal structure it has been degraded to $C_{22}H_{44}O_2$ (A., 1904, i, 548; 1905, i, 405, 736), and attempts have also been made to synthesise it from normal behenic acid, $C_{22}H_{44}O_2$. The degradation product is not identical with behenic acid, and the synthetic product is not lignoceric acid, so that the latter cannot be the normal 24 carbon saturated fatty acid.

Lignoceric acid, $C_{24}H_{48}O_2$, m. p. 80—80·5°, prepared from ground-nut oil, on treatment with bromine in presence of amorphous phosphorus yields *α-bromolignoceric acid*, m. p. 68·5°, which crystallises in colourless rhombohedra and on treatment with sodium ethoxide in dry alcohol furnishes with some difficulty *α-ethoxylignoceric acid*, m. p. 61—62°, crystallising in slender, colourless needles. *Methyl α-bromolignocerate*, m. p. 46—47°, forms small, colourless crystals. The bromo-acid when boiled with potassium iodide in alcohol yields *α-iodolignoceric acid*, m. p. 74°, which forms small, colourless prisms from a mixture of light petroleum and acetic acid, and when treated with potassium

hydroxide furnishes a mixture of *α-hydroxylignoceric acid* (m. p. 92°, small crystals) with the *unsaturated acid*, $C_{24}H_{46}O_2$, m. p. 59°, which forms a crystalline mass. The latter acid on oxidation with permanganate yields oxalic acid and *isobehenic acid*, $C_{22}H_{44}O_2$, m. p. 75°. The latter crystallises in glancing pearly leaflets, and furnishes a *methyl* ester, m. p. 54°, as colourless leaflets, and a crystalline *lithium* salt, m. p. 210° (decomp.). Melting-point curves for mixtures (1) of behenic and *iso*behenic acids, and (2) of the methyl esters of the two acids are given.

Behenic acid, m. p. 82—84°, was prepared by the catalytic reduction of erucic acid, and converted successively into the chloride (leaflets, m. p. 73—75°); methyl ester, m. p. 55°; amide, m. p. 111°, and the latter reduced to docosyl alcohol by means of sodium in amyl alcohol and this was converted into docosyl iodide, m. p. 46°. The latter was condensed with ethyl malonate to *docosylmalonic acid*, and this heated until carbon dioxide was no longer evolved when it yielded a *tetracosanic acid*, $C_{24}H_{48}O_2$, m. p. 85·5—86°, crystallising in pearly leaflets, and furnishing a *methyl* ester (m. p. 59·5—60°, glancing scales), a crystalline *lithium* salt, and an *α-bromo*-derivative, m. p. 73·5°, the *methyl* ester of which has m. p. 57°, and crystallises in glancing leaflets. Melting-point curves and tables for mixtures (1) of synthetic tetracosanic acid and lignoceric acid, and (2) of the methyl esters of these two acids are given.

In the synthesis of the tetracosanic acid the principal product is a *ketone*, $C_{47}H_{94}O$, which was not further characterised.

The synthetic method described was also used in preparing arachidic acid, m. p. 77°, from octadecyl iodide (compare Baczewski, A., 1897, i, 11). Melting-point curves for mixtures of lignoceric acid with (*a*) arachidic acid, (*b*) stearic acid, and (*c*) palmitic acid are given.

T. A. H.

Montanic Acid. HANS MEYER and LEO BROD (*Monatsh.*, 1913, **34**, 1143—1157. Compare Easterfield and Taylor, T., 1911, 99, 2302).—Montanic acid has been exhaustively examined and purified by methods described in detail in the original, and shown to have the formula, $C_{28}H_{56}O_2$, first suggested by Ryan and Dillon (A., 1909, i, 629). A number of its derivatives are described.

Montanic acid melts at 85° and crystallises from acetic acid in small, pearly leaflets. The *chloride*, m. p. 67·5—68·5°, forms masses of leafy crystals and is readily soluble in benzene or petroleum. The *amide*, m. p. 112°, separates from alcohol as a crystalline powder. *α-Bromomontanic acid*, m. p. 77°, forms colourless scales from a mixture of acetic acid and light petroleum; with sodium ethoxide in alcohol, it yields *α-ethoxymontanic acid*, m. p. 71—72°, crystallising from acetic acid in colourless scales, and with ethyl alcohol in presence of mineral acids, *ethyl bromomontanate*, m. p. 62—63°, which forms colourless leaflets from alcohol. Attempts to eliminate hydrogen bromide and form the corresponding unsaturated acid were successful. T. A. H.

Ground-nut (Earth-nut) Oil. HANS MEYER and ROBERT BEER (*Monatsh*, 1913, **34**, 1195—1268).—The numerous researches already

conducted on the composition of ground-nut oil render it probable that it contains glycerides of arachidic, lignoceric, oleic and linoleic acids, and leave doubtful the presence of glycerides of palmitic, stearic, and hypogaeic acids. The authors confirm the occurrence in the oil of glycerides of the four first-named acids and also of palmitic acid, but they were unable to find any evidence of stearic or hypogaeic acid in the fatty acids prepared from the oil (compare Franz, *Diss.*, München, 1910). The supposed stearic acid obtained by Hehner and Mitchell's method (A., 1897, ii, 289) lowers the melting point of stearic acid and in reality consists of a mixture of arachidic and lignoceric acids. No trace of dihydroxypalmitic acid could be found in the oxidation products from the unsaturated fatty acids of ground-nut oil so that hypogaeic acid cannot be a constituent of these acids. Tables and curves of the melting points of mixtures of arachidic acid with (*a*) stearic acid and (*b*) palmitic acid are given in the original.

T. A. H.

Candelilla Wax. HANS MEYER and WALTHER SOYKA (*Monatsh.*, 1913, 34, 1159—1172. Compare Olsson-Seffer, *Bull. Imp. Inst.*, 1909, 7, 411; Hare and Bjerregard, *J. Ind. Eng. Chem.*, 1910, 2, 203; Delcr. *ibid.*, p. 454; Sanders, P., 1911, 27, 250, and *Anal. Inst. Nac. Med. Mex.*, 1905, 7, 498, and Niederstadt, *Chem. Zeit*, 1911, 35, 1190).—Candelilla wax on extraction with hot alcohol yields 18 to 20% of soluble soft resin, which gives the Liebermann-Storch reaction. The portion of the resin-free wax soluble in hot alcohol, but insoluble in the cold, consists principally of dotriacontane, not hentriacontane as Sanders (*loc. cit.*) supposed, which was isolated by extraction with ether and amounted to 74 to 76% of the crude wax. The remaining constituent not removed by ether is a lactone, $C_{30}H_{58}O_3$, m. p. 88°, which forms a colourless, crystalline mass, is neutral in reaction, but yields a *potassium* salt when boiled with potassium hydroxide in alcohol, and is partly esterified when treated with methyl alcohol and sulphuric acid. This substance appears to be that which Sanders mistook for myricyl alcohol (*loc. cit.*), and which Fraps and Ruther (*J. Ind. Eng. Chem.*, 1910, 2, 454) described as a hydrocarbon. It is perhaps identical with Darmstädter and Lifschütz's lanoceric acid lactone (A., 1896, i, 522).

The authors doubt whether the hydrocarbon frequently found in plants and described as hentriacontane really consists of the latter.

T. A. H.

Water of Crystallisation of the Calcium Salt of Lauronolic Acid. CHARLES E. BURKE (*J. Amer. Chem. Soc.*, 1913, 35, 1647—1648).—Although the rapid evaporation of a solution of calcium lauronolate on a water-bath gives surface crystals containing approximately $3H_2O$ (Noyes and Burke, A., 1912, i, 159), yet under the conditions of Bredt's method with slower evaporation (A., 1911, i, 417) the crystals, which separate in this case under the liquid, contain exactly $2H_2O$, as stated by Bredt. D. F. T.

Preparation of Di-iodotariric Acid. F. HOFFMANN-LA ROCHE & Co. (D.R.-P. 261211. Compare A., 1892, 470).—*Di-iodo-*

tariric acid, colourless needles, m. p. 48·5°, containing 47·5% of iodine and of therapeutic value, is obtained when a boiling aqueous solution of tariric acid containing sodium hydroxide is slowly treated with 3 parts of a mixture of iodine (100 parts), potassium iodide (160 parts), and water (740 parts); the product is separated by the addition of dilute sulphuric acid. F. M. G. M.

The Ability of Alcoholic Hydroxyl Groups to Form Complexes. II. GENNARO CALCAGNI (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 157—162. Compare A., 1910, i, 811; Weinland and Herz, A., 1912, i, 854).—The *basic glycollate* of a *hexaglycollatotriferri*-base, $[Fe_3(OH)_2(CO_2\cdot CH_2\cdot OH)_6]\cdot CO_2\cdot CH_2\cdot OH(FeOH)_3$, prepared by fractional precipitation of an alcoholic solution with ether, is an orange-yellow, amorphous substance which is hygroscopic and readily hydrolysed. The *basic nitrate*, $[Fe_3(OH)_2(CO_2\cdot CH_2\cdot OH)_6]NO_3\cdot Fe(OH)_3$, is similar in properties. The *basic lactate* of a *hexalactatotriferri*-base,

$$[Fe_3(OH)_2(CO_2\cdot CHMe\cdot OH)_6]CO_2\cdot CHMe\cdot OH\cdot Fe(OH)_3,4H_2O,$$

is an orange-yellow, hygroscopic substance which is readily hydrolysed.

When solutions of chrome alum and sodium benzoate are mixed, *chromous benzoate*, $Cr(CO_2Ph)_2,H_2O$, is precipitated. *Ferrous salicylate*, $Fe(CO_2\cdot C_6H_4\cdot OH)_2$, is a reddish-violet, amorphous substance. *Chromous salicylate* was also prepared. R. V. S.

Complex Oxalic Derivatives of Iridium. ALEXIS DUFFOUR (*Ann. Chim. Phys.*, 1913, [viii], **30**, 169—240).—A detailed, connected account of work already published (Abstr., 1909, i, 762—763; 1910, i, 541; 1911, i, 519; 1912, ii, 849). Apart from slight modifications of some of the views expressed already, the following new results are now recorded. *Thallous iridotetrachloro-oxalate*, $Tl_2IrCl_4C_2O_4$, forms maroon-coloured, microscopic, hexagonal lamellæ, which are pleochroic and faintly birefringent. *Argentous iridotetrachloro-oxalate* resembles the thallous salt, but only assumes a crystalline texture after prolonged contact with water. T. A. H.

Electrolytic Reduction of Aldehydes. WILHELM SCHEPSS (*Ber.*, 1913, **46**, 2564—2574).—An extension of the earlier investigation (Tafel and Schepss, A., 1911, i, 784) in which it was demonstrated that by electrolytic reduction the aldehyde group in anisaldehyde can be directly converted into the methyl group. The reduction of the aldehydes was effected in a mixture of alcohol and sulphuric acid.

Propaldehyde undergoes reduction to propane less readily than does acetone, and it was found that cathodes of lead or cadmium are much more effective than a mercury cathode. No formation of any organic lead or mercury compounds analogous to those observed in the reduction of acetone could be detected.

Reduction of heptaldehyde yielded *n*-heptane, and again the action proceeds less easily than with methyl *iso*amyl ketone (Tafel, A., 1909, i, 766). Benzaldehyde (compare Kauffmann, A., 1899, i, 152; Law, T., 1907, **91**, 755) at a cadmium cathode gave as hydrocarbon product a small quantity of toluene; no benzene could be detected (compare

Law, *loc. cit.*). *p*-Hydroxybenzaldehyde could be reduced to *p*-cresol; salicylaldehyde and *m*-hydroxybenzaldehyde appeared to undergo reduction only as far as the corresponding alcohols, and in attempts to reduce the former more energetically much resinification occurred.

Protocatechualdehyde gave 3 : 4-dihydroxytoluene, whilst vanillin gave the corresponding ether, 4-hydroxy-3-methoxytoluene. The experiments in the latter case were conducted with cadmium electrodes and the result is somewhat at variance with that of Law (*loc. cit.*). Piperonal underwent reduction to hydropiperoin and *methylenedioxytoluene*, an aromatic oil, b. p. 81—83°/11 mm., 197—198° (corr.)/745·5 mm., D_{15}^{15} 1·1353, n_D^{15} 1·53165.

When reduced in solution in the usual mixture of alcohol and sulphuric acid, *p*-dimethylaminobenzaldehyde was converted into the corresponding alcohol, which immediately condensed with the alcohol of the solvent; the product was therefore p-*dimethylaminobenzyl ethyl ether*, $NMe_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}OEt$, a liquid of characteristic amine odour, b. p. 269—271°/747 mm.; *methiodide*, m. p. 141·5—143°. Reduction of the aldehyde in alcohol-free diluted sulphuric acid gave as chief product *p*-dimethylaminobenzyl alcohol, as a viscous oil, b. p. 175—178°/25 mm. (compare Rousset, A., 1895, i, 176).

In the above examples it was generally found that the process of reduction became more speedy and complete with increased temperature and current density. The extent to which reduction was effected varied considerably, however, in different cases.

A repetition of the reduction of citral (Law, T., 1912, **101**, 1025, 1544) at a lead cathode certainly yielded a red product at the cathode, but it was of a resinous nature and not an organic lead compound. D. F. T.

Formation of Methylglyoxal. CARL NEUBERG and W. OERTEL (*Biochem. Zeitsch.*, 1913, **55**, 495—503).—The importance of methylglyoxal as an intermediary product of sugar degradation has been often discussed, and the substance has been obtained directly from dextrose by various methods (distillation in presence of weak alkalis, zinc carbonate, etc.). It is now shown that it can be obtained from sugars in larger quantities if solutions of these substances are heated with sodium carbonate or disodium hydrogen phosphate in the presence of phenylhydrazine. Particularly good yields were obtained in this way from lævulose, and moderate yields from dextrose. Mannose also yielded a small quantity. The methylglyoxal was in each case identified in the form of an osazone. S. B. S.

Plant Colloids. III. Processes of Solution and Removal of the Ash of Starch. MAXIMILIAN SAMEC and F. VON HOEFFT (*Koll. Chem. Beihefte*, 1913, **5**, 141—210. Compare A., 1912, ii, 144).—The influence of the removal of the ash from starch on the physicochemical properties of starch solutions has been studied, and the properties of solutions of such starch are compared with those of ordinary starch solutions prepared under identical conditions. It is shown that the three processes, removal of the ash, solution and ageing

occasion the same changes in the properties of starch solutions, namely, decrease of the viscosity, and decrease of the influence of acids and bases on the viscosity. These changes take place more rapidly the higher the temperature. At constant temperature in solutions of different concentrations the viscosity decreases in the same proportion in the same time. Simultaneously with the decrease of viscosity an increase in the electrical conductivity is brought about, and the electric transport and amount precipitated by alcohol decrease. The osmotic pressure is slightly decreased, whilst the optical rotation slightly increases and the quantity of titratable acid increases. Starch granules give practically no free electrolyte to water at ordinary temperatures, but at the swelling temperature this occurs fairly rapidly, and at the same time the power of the granules for taking up water increases in a series of sudden steps. The observations lead to the assumption that the ash of starch is present as an amylphosphoric acid, and this assumption brings observations of other observers into agreement. J. F. S.

Chemistry of Starch. Schardinger's Crystalline Dextrins. II. HANS PRINGSHEIM and FRANZ EISSLER (*Ber.*, 1913, **46**, 2959—2974. Compare A., 1912, i, 832).—Further observations on dextrin-β (hexa-amylose), dextrin-α (tetra-amylose), and their scission products are recorded and the properties of the crystalline "slime" prepared by Schardinger are described. Provisional formulæ for diamylose and *iso*-diamylose are advanced and discussed.

Schardinger's "slime" $[(C_6H_{10}O_5)_2]_x,C_2H_5{\cdot}OH$, was prepared by dissolving crude dextrin (precipitated by means of chloroform from the liquid produced by the action of *Bacillus macerans* on starch paste) in hot water, heating to remove chloroform and then diluting with water, when the slime was precipitated. It was isolated by means of a centrifuge, and crystallised from water containing 1·5% alcohol, when it formed hexagonal tablets. It has $[\alpha]_D^{20}$ $+139·2°$. On acetylation in presence of zinc chloride, it yields the hexa-acetate of diamylose (*loc. cit.*) and by the Baumann-Schotten method yields the *dibenzoate* of *diamylose*, m. p. 200° (approx.), an amorphous substance also obtained when tetra-amylose is benzoylated by this process, an observation which indicates that the slime belongs to the α-group of dextrins. Triamylose, the scission product of dextrin-β, yields a *tribenzoate*, m. p. 190°, which is also amorphous.

These amyloses (dextrins) all yield additive products with iodine when their aqueous solutions are treated with iodine in potassium iodide. The iodine additive products of the α-group form green-tinted needles, become blue when moistened with water, but form dark red solutions when much water is added; those of the β-group form dark reddish-brown prisms and give dark red solutions with water. *Tetra-amylose iodide*, $(C_6H_{10}O_5)_4,1\frac{1}{2}I$, and *hexa-amylose di-iodide*, $(C_6H_{10}O_5)_6,2I$, belonging respectively to these groups, have been prepared; the slime gives an iodide of the α-type.

When tetra-amylose is dissolved in glycerol by heating, and the liquid is heated at 200° during thirty minutes, a small part of the dextrin is converted into the slime and a little into *isodiamylose*, a new

amorphous amylose of the β-type. The latter is also obtained in the form of its amorphous *hexa-acetate* when tetra-amylose is acetylated with acetic anhydride in presence of sulphuric acid. Similarly, hexa-amylose when heated in water for a long time yields a small amount of the slime, and when acetylated in presence of sulphuric acid yields *isotriamylose-nonoacetate*, from which on hydrolysis iso*triamylose* is obtained; both these products are also amorphous. These new amyloses are hygroscopic, dextrorotatory, decompose without melting when heated, and reduce Fehling's solution. Some preliminary observations on the acetylation of "soluble" starch are also recorded.

Starch was separated by Gatin-Grużewska's method (A., 1911, i, 551) into amylopectin and Maquenne's amylose. These two products on treatment with *Bacillus macerans* fermented less easily than starch, but yielded the same products, viz., tetra-amylose, hexa-amylose, and the slime.

Takadiastase and *Penicillium africanum* hydrolyse hexa-, tetra-, tri-, and di-amyloses, whilst emulsin decomposes *iso*tri- and *iso*di-amyloses, but has no action on the other four. Yeast and diastase do not act on any of the six dextrins. T. A. H.

Hexabromoplatinates [Platinibromides]. ALEXANDER GUTBIER and A. RAUSCH (*J. pr. Chem.*, 1913, [ii], 88, 409—424. Compare A., 1910, i, 12; 1911, i, 32).—On account of their sparing solubility and superior powers of crystallisation, the platinibromides may be employed with advantage for the characterisation of amines in place of the platinichlorides.

A solution of hydrogen platinibromide, suitable for this purpose, is readily obtained by dissolving platinic chloride in 20—30 times its weight of hydrobromic acid (D 1·49), and evaporating its solution to half its bulk.

The platinibromides have no definite m. p., but become dark and sinter before liquefaction takes place.

The compounds described below form light red to dark red crystals having a magnificent lustre:

Tetramethylammonium platinibromide, $(NMe_4)_2PtBr_6$, lustrous, red crystals of octahedral habit. *Tetraethylammonium platinibromide*, felted crystals.

Tripropylammonium platinibromide, compact clusters of deep red, rhombic, double pyramids.

Diisobutylammonium platinibromide, elongated prisms. *Triisobutylammonium platinibromide*, small, red crystals. iso*Amylammonium platinibromide*, bright red crystals. *Diisoamylammonium platinibromide*, tabular crystals. *Triisoamylammonium platinibromide*, bright red prisms. *Allylammonium platinibromide*. *Guanidine platinibromide*, $C_2H_{12}N_6PtBr_6$, lustrous, red crystals of a complicated structure. *Triphenylguanidine platinibromide*,

$$2NPh:C(NHPh)_2,H_2PtBr_6,$$

slender, felted, orange-red needles.

Nitrosodimethylammonium platinibromide, $(NO\cdot NHMe_2)_2PtBr_6$, acicular, pleochroic prisms. *Nitrosodiethylammonium platinibromide*, dark red, fibrous crystals. *Nitrosodipropylammonium platinibromide*,

red prisms. *Nitrosodiisobutylammonium platinibromide*, dark red felted crystals.

m-*Chlorophenylammonium platinibromide*, $(C_6H_4Cl\cdot NH_3)_2PtBr_6$, lustrous, red plates. p-*Chlorophenylammonium platinibromide*, bright red, elongated prisms. 2 : 4-*Dichlorophenylammonium platinibromide*, dark red platelets.

o-*Bromophenylammonium platinibromide*, prisms combined with pyramids. m-*Bromophenylammonium platinibromide*, small, dark red, felted crystals. p-*Bromophenylammonium platinibromide*, red, fibrous crystals.

m-*Nitrophenylammonium platinibromide*, prisms. p-*Nitrophenylammonium platinibromide*, elongated prisms. p-*Nitrosophenyldimethylammonium platinibromide*, $(NO\cdot C_6H_4\cdot NHMe_2)_2PtBr_6$, deep red, felted crystals.

o-*Tolyldimethylammonium platinibromide*, $(C_6H_4Me\cdot NHMe_2)_2PtBr_6$, lustrous, red plates.

p-*Tolyldimethylammonium platinibromide*, red plates. 2 : 4-*Tolylenediammonium platinibromide*, $C_7H_{12}N_2PtBr_6$, deep red prisms. 3 : 4-*Tolylenediammonium platinibromide*, vivid red prisms.

o-*Methoxyphenylammonium platinibromide*, vivid red, monoclinic prisms. p-*Methoxyphenylammonium platinibromide*, long, slender, lustrous, red prisms. o-*Ethoxyphenylammonium platinibromide*, stellar, feebly pleochroic discs, or long prisms. p-*Ethoxyphenylammonium platinibromide*, lustrous, red, fibrous crystals.

Tribenzylammonium platinibromide, dark red crystals. *Benzylmethylammonium platinibromide*, dark red prisms.

Benzylidenemethylammonium platinibromide,

$$(CHPh:NHMe)_2PtBr_6,$$

red, felted aggregates. *Benzylidene-ethylammonium platinibromide*, leaflets.

Phenylbenzylammonium platinibromide, dark red crystals. *Phenylbenzylmethylammonium platinibromide*, $(NHMePh\cdot C_7H_7)_2PtBr_6$, red, felted crystals. *Phenylbenzylideneammonium platinibromide*, elongated prisms. 2 : 4 : 5-*Trimethylphenylammonium platinibromide*, light red prisms.

3-*Methylpyridinium platinibromide*, dark red, regular crystals. *Dimethylpyridinium platinibromide*, dark red, felted crystals. *Trimethylpyridinium platinibromide*, clusters of deep red crystals. *Piperidinium platinibromide*, elongated prisms. iso*Quinolinium platinibromide*, lustrous, red, prismatic crystals. F. B.

Action of Ammonia on β-Aminocrotonates and β-Carbethoxyaminocrotonates. Ernst Philippi (*Monatsh*, 1913, 34, 1187—1193. Compare this vol., i, 598).—It is argued that the substance which Meister (A., 1888, 675) regarded as having the formula $OEt\cdot C(OH)(NH_2)\cdot CH:CMe\cdot NH\cdot CO\cdot NH_2$, may be equally well represented by the formula

$$CH_3\cdot CH(NH\cdot CO\cdot NH_2)\cdot CH(NH_2)\cdot CO_2Et$$

or $CH_3\cdot C(NH_2)(NH\cdot CO\cdot NH_2)\cdot CH_2\cdot CO_2Et$, so far as the reactions described by Meister are concerned. The author finds that the substance on treatment with hot alkali solution yields ethyl β-amino-

crotonate, and that the latter condenses with carbamide in dry alcohol to regenerate the parent substance, which must therefore be ethyl β-amino-β-carbamidobutyrate represented by the third formula given above.

It is remarkable that whilst the substance is formed by the action of alcoholic ammonia at 160—170° on ethyl β-aminocrotonate, it is not produced when liquefied ammonia is allowed to react with the ester in the cold even for several days. It is probable that in the former case part of the ester is decomposed with the formation of carbamide, which then condenses with the rest of the ester. T. A. H.

The Condensation of Carbamides with Esters. GEORG ROEDER (*Ber.*, 1913, 46, 2560—2564).—In an attempt to prepare hydurilic acid from ethyl ethanetetracarboxylate and carbamide, Conrad (A., 1907, i, 985) obtained scarcely a trace of the desired substance, although the analogous reaction with guanidine in place of carbamide proved satisfactory. It is now shown that the reaction with carbamide follows a different course from that expected, giving rise to *ethanetetracarboxylimide*, which carbonises at 270°. The reaction was effected in warm alcoholic solution containing sodium ethoxide, and can be represented as: $CH(CO_2Et)_2 \cdot CH(CO_2Et)_2 + 2CO(NH_2)_2 =$

$$NH{<}{\begin{matrix}CO\cdot CH\cdot CO\\ CO\cdot CH\cdot CO\end{matrix}}{>}NH + 2NaOCN + 4EtOH.$$

With thiocarbamide, the ester behaves as ethyl dimalonate, and under similar conditions to the last gives rise to *dithiohydurilic acid*, according to the equation: $CH(CO_2Et)_2 \cdot CH(CO_2Et)_2 + 2CS(NH_2)_2 = CS{<}{\begin{matrix}NH\cdot CO\\ NH\cdot CO\end{matrix}}{>}CH\cdot CH{<}{\begin{matrix}CO\cdot NH\\ CO\cdot NH\end{matrix}}{>}CS + 4EtOH$; the product, which is unaltered at 250°, gives a yellow *pyridine* salt, and when suspended in water is coloured green by ferric chloride; it can be desulphurised to hydurilic acid by heating at 100° with concentrated sulphuric acid.

As might be expected from the above results, ethyl succinate condenses with carbamide under similar conditions to the above with formation of succinimide and sodium cyanate. It is suggested that in this and the analogous case above, the course of the reaction follows the stages: $CH_2(CO_2Et) \cdot CH_2 \cdot CO_2Et \longrightarrow {\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CO\end{matrix}}{>}N\cdot CO\cdot NH_2 \longrightarrow {\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CO\end{matrix}}{>}NH + NH_2\cdot CO_2Et$; the last substance, the formation of which is attributed to the action of the alcohol on the primary condensation product, then decomposes under the influence of sodium ethoxide into alcohol and sodium cyanate.

When ethyl phthalate is subjected to this reaction, either with carbamide or thiocarbamide, the product is phthalimide. D. F. T.

Chloro-glyoxime, Oxime Derivatives of Oxalyl Chloride and Oxalyl Semichloride, and Cyanoformylchloride Oxime. JOSEF HOUBEN and H. KAUFFMANN (*Ber.*, 1913, 46, 2821—2835).—By careful chlorination in cold hydrochloric acid solution, both chloro-

amphi- and chloro-*anti*-glyoxime are converted into the same dichloro-*anti*-glyoxime. The chloro-*anti*-glyoxime is the more readily chlorinated. It is established that fuming hydrogen chloride converts chloro-*amphi*-glyoxime into the *anti*-modification contrary to the statement of Hantzsch, (A., 1892, 693).

Dichloro*anti*glyoxime, OH·N:CCl·CCl:N·OH, has decomp. 221 when crystallised from water, or 212° when crystallised from toluene. It gives a reddish-brown coloration with ferric chloride.

Dichloroglyoxime diacetate, OAc·N:CCl·CCl:N·OAc, separates in well formed crystals, m. p. 162—163°. Dry ammonia gas converts it into dioximino-ethylenediamine, which differs from the known compound, firstly, in forming a *diacetyl* derivative, m. p. 206° when crystallised from water, or 212° when crystallised from chloroform, and secondly, in not yielding a dibenzoyl derivative. The difference is attributed to a changed configuration.

Thionyl chloride converts chloro*amphi*glyoxime into *chloro-oximino-acetonitrile*, OH·N:CCl·CN. This is purified by distillation and the crystals formed, which are extremely hygroscopic, filtered and dried in a current of air in a specially constructed apparatus. It has m. p. 55—56°; the vapour has a very irritant action. It crystallises in monoclinic prisms and plates giving no coloration with ferric chloride until it has been warmed with water for a few seconds. The substance is a mixture of the two forms: $\begin{array}{c}\mathrm{Cl\cdot C\cdot CN}\\ \Vert \\ \mathrm{HO\cdot N}\end{array}$ and $\begin{array}{c}\mathrm{Cl\cdot C\cdot CN}\\ \Vert \\ \mathrm{N\cdot OH}\end{array}$, in which one greatly preponderates. The form present in the smaller proportion is much more easily decomposed by water. Probably the conversion of one form into the other takes place during the distillation.

Solution of the nitrile in water yields very soon a voluminous, flocculent precipitate which does not contain halogen. Its investigation is not yet completed, but it is probably *dioximino-oxalonitrile* NC·C(N·OH)·C(N·OH)·CN. It explodes violently at 250—260°.

Whereas both chloro-*amphi*- and *anti*-glyoxime diacetate and chloro-*amphi*-glyoxime monoacetate distil unchanged in a vacuum, the *anti*-diacetate at the ordinary pressure is decomposed, losing acetic acid and forming *chloro-oximinoacetonitrile acetate*, CN·CCl:N·OAc, a clear liquid, b. p. 74—75°/13 mm.

Fuming hydrochloric acid converts it into *chloro-oximinoacetamide*, OH·N:CCl·CO·NH_2, which crystallises in well-formed, pointed needles, m. p. 162°, crystallised from water, or 166° crystallised from benzene (decomp.).

On acetylation, *acetoximinochloroacetamide*, OAc·N:CCl·CO·NH_2, m. p. 134°, is formed. This compound serves to distinguish the oximinoacetamide from the chloroglyoximes.

The *hydrochloride* of *chloro-oximinoacetiminomethyl ether*,

OH·N:CCl·CCl(NH_2)·OMe,

forms crystals, m. p. 161°. The analogous *ethyl* ether has m. p. 155—164° according to the rate of heating.

When hydrolysed in fuming hydrochloric acid, *chloro-oximinoacetic acid*, OH·N:CCl·CO_2H, is formed. This has m. p. 125° (decomp.)

The acid is also obtained from chloro-oximinoacetic ester as prepared by Jovitschitsch (A., 1906, i, 732).

It has a strong acid astringent and yet sweet taste. It gives a deep dark red coloration with ferric chloride. E. F. A.

Crystals of Diamminedimethylglyoximinecobalt Chloride. D. N. Artemév (*Zeitsch. Kryst. Min.*, 1913, **52**, 632; from *Ann. Inst. Mines, St. Petersburg*, 1910, **2**). **Crystals of Chloroammine-dimethylglyoximinecobalt.** D. N. Artemév and D. Th. Muraschev (*ibid.*, 1913, **52**, 627—628; from *ibid.*, 1910, **2**, 272—274). **Crystals of Nitroaquodimethylglyoximinecobalt.** D. N. Artemév and W. M. Lomberg (*ibid.*, 1913, **52**, 632—633; from *ibid.*, 1910, **2**, 352—356).—Descriptions are given, in Fedorov's nomenclature, of the crystals of these compounds prepared by L. A. Tschugaev (A., 1906, i, 814). Their formulæ are respectively $Co(NH_3)_2D_2H_2Cl,5H_2O$, $CoNH_3ClD_2H_2$, and $CoNO_2D_2H_2,H_2O$, where $D = \begin{matrix} CH_3\cdot C{:}NO \\ | \\ CH_3\cdot C{:}NO \end{matrix}$. L. J. S.

Complex Compounds of Rhodium. Leo A. Tschugaev and W. Lebedinski (*Zeitsch. anorg. Chem.*, 1913, **83**, 1—7).—Rhodium forms complex compounds with α-dioximes, completely resembling those of tervalent cobalt (A., 1906, i, 814; 1907, i, 904). Two series of compounds are formed, one being salts of a mono-acid base, $[Rh,2NH_3,D_2H_2]X$, and the other salts of a monobasic complex acid, $[RhCl_2,D_2H_2]H$ (D = dimethylglyoxime, X = halogen). The complex acid is remarkably stable.

Diamminedimethylglyoximinerhodium chloride,

$$[Rh,2NH_3,D_2H_2]Cl,5H_2O,$$

from dimethylglyoxime and chloropentamminerhodium chloride at 150°, crystallises from hot water. The *iodide* is anhydrous. The *nitrate* is precipitated in microscopic tablets; the *perchlorate*, *platinichloride*, and *platinibromide* are very insoluble.

Rhodidichlorodimethylglyoximinic acid, $[RhCl_2,D_2H_2]H$, from sodium rhodihexachloride and dimethylglyoxime, boiled with water, crystallises from water containing a little hydrochloric acid. The *ammonium* salt, with $1H_2O$, forms large, brownish-yellow crystals. The *guanidinium* salt is anhydrous and sparingly soluble. C. H. D.

Decomposition of Alkylidenehydrazines. Nicolai M. Kishner (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 973—986).—The action of magnesium methyl iodide on *cyclo*butanecarboxylamide yields acetyl*cyclo*butane, b. p. 137—139°/761 mm., and the latter, on decomposition of its hydrazone, gives *ethylcyclobutane*, $CH_2<\substack{CH_2 \\ CH_2}>CHEt$, b. p. 70°/754 mm., D_0^0 0·7461, D_0^{20} 0·7284, n_D^{15} 1·4032, n_D^{20} 1·4004, which is extremely stable towards permanganate, towards fuming hydrobromic acid in a sealed tube at 100°, and unlike derivatives of three-membered rings, towards concentrated sulphuric acid at the ordinary temperature. Reduction of ethyl*cyclo*butane by means of fuming hydriodic

acid in a sealed tube at 210° yields γ-methylpentane, but no *n*-hexane; as would be expected from the presence of a CH-group in the molecule, γ-methylpentane is readily attacked by fuming nitric acid.

1 : 1-Dimethyl*cyclo*pentane (compare A., 1908, i, 864) may be obtained by distilling 1 : 1-dimethyl-2-*cyclo*pentanonehydrazone (A., 1911, i, 42) with potassium hydroxide and platinised porous tile.

Allylacetonehydrazone [Δ^{α}-*hexylen-ε-onehydrazone*],

$$CH_2\colon CH\cdot CH_2\cdot CH_2\cdot CMe\colon N\cdot NH_2,$$

b. p. 187—188°/757 mm., $D_0^{17.5}$ 0·8990, mixes with water in all proportions and, when distilled with potassium hydroxide and platinised porous tile, yields Δ^{α}-*hexene*, $CH_2\colon CH\cdot CH_2Pr$, b. p. 64°/756 mm., D_0^{20} 0·6734, n_D^{20} 1·3870.

Distillation of β-methyl-Δ^{β}-hepten-ζ-onehydrazone with potassium hydroxide and platinised porous tile yields *β-methyl-*Δ^{β}*-heptene*, $CMe_2\colon CH\cdot CH_2Pr$, b. p. 122·4°/756 mm., D_0^{20} 0·7254, n_D^{20} 1·4169, which gives β-methylheptane (compare Clarke, A., 1911, i, 345) on reduction by Sabatier and Senderens' method, and forms the *nitrosochloride*, $CMe_2Cl\cdot C(\colon NOH)\cdot CH_2Pr$, m. p. 48—51°, this exhibiting normal cryoscopic behaviour in benzene. By removal of hydrogen chloride from the nitrosochloride, conversion of the oxime thus obtained into the corresponding ketone, and distillation of the hydrazone of this ketone with potassium hydroxide and platinised porous tile, β-methyl-Δ^{β}-heptene is again obtained.

Distillation of pentan-α-ol-δ-onehydrazone gives *n*-amyl alcohol.

βζ-Dimethyl-Δ^{β}-octene, $CMe_2\colon CH\cdot CH_2\cdot CH_2\cdot CHMeEt$, obtained by distillation of the hydrazone of the keto-alcohol,

$$OH\cdot CMe_2\cdot CO\cdot CH_2\cdot CH_2\cdot CHMeEt$$

(A., 1911, i, 1027), with potassium hydroxide and platinised porous tile, seems to be identical with the hydrocarbon obtained from citronellaldehydehydrazone (A., 1911, i, 1027). T. H. P.

Complex Mercury Compounds from Ethylene and Carbon Monoxide. WALTER SCHOELLER, WALTER SCHRAUTH, and WALTER ESSERS (*Ber.*, 1913, **46**, 2864—2876).—Mercury acetate in methyl alcohol reacts with a molecule of ethylene to form *acetatomercuriethyl methyl ether*, $CH_3\cdot CO\cdot O\cdot Hg\cdot CH_2\cdot CH_2\cdot OMe$, crystallising in colourless, slender, pointed needles, m. p. 42°. The *bromide* of the ether forms bunches of needles, m. p. 58°; the *iodide* crystallises in stellate aggregates of needles or platelets.

In presence of ethyl alcohol reaction between the mercury salt and ethylene is slower, and *acetatomercuridiethyl ether*,

$$CH_3\cdot CO\cdot O\cdot Hg\cdot C_2H_4\cdot OEt,$$

is formed. This sinters at 33°, m. p. 36°. The *chloride* crystallises in colourless needles, m. p. 92°.

When carbon monoxide is substituted for ethylene, *methyl acetatomercuriformate*, $CH_3\cdot CO\cdot O\cdot Hg\cdot CO\cdot OMe$, is formed. It crystallises in stellate aggregates of needles, m. p. 110° (corr. decomp.). The *chloride* separates in long needles, m. p. 110° (corr. decomp.); the *bromide* is composed of colourless platelets, decomp. 127—128°, and the *iodide* is similar in appearance.

Treatment with hydrogen sulphide in methyl alcohol gives rise to

the formation of *methyl sulphidomercuriformate*, $S(Hg{\cdot}CO{\cdot}OMe)_2$, obtained as a colourless, cheese-like precipitate.

Mercuric acetate ethyl formate crystallises in aggregates of needles which sinter at 65°, decomp. 125°. The *chloride* forms plates, m. p. 85° (corr., decomp.); the *bromide* and *iodide* are very similar. The *sulphide* was obtained as a yellowish-white precipitate. E. F. A.

Decomposition of Pyrazoline Bases. Conversion of Phorone into 1 : 1-Dimethyl-2-*iso*butenyl*cyclo*propane. NICOLAI M. KISHNER (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 957—972).—The similarity in structure between mesityl oxide and phorone suggests the possibility of transforming the latter ketone into a pyrazoline base and thence into a hydrocarbon containing a trimethylene ring (compare A., 1912, i, 215). This possibility has been realised by the author.

Phorone and hydrazine react according to the equation:

$$CMe_2{:}CH{\cdot}CO{\cdot}CH{:}CMe_2 + N_2H_4 \longrightarrow CMe_2{:}CH{\cdot}C{<}\begin{matrix}CH_2{\cdot}CMe_2\\ N{-\!-}NH\end{matrix}.$$

When distilled with potassium hydroxide in presence of platinised porous tile, this pyrazoline base decomposes in two ways, giving (1) 1 : 1-dimethyl-2-*iso*butenyl*cyclo*propane, or (2) the trimethylpyrazoline and acetone, $CMe{<}\begin{matrix}CH_2{\cdot}CMe_2\\ N{-\!-}NH\end{matrix} + COMe_2$.

1 : 1-*Dimethyl*-2-iso*butenyl*cyclo*propane*, $CH_2{<}\begin{matrix}CMe_2\\ CH{\cdot}CH{:}CHMe_2\end{matrix}$, is a liquid, b. p. 132°/758 mm., D_0^{20} 0·7677—0·7681, n_D 1·4414—1·4420. Although the chemical properties of this hydrocarbon are in complete accord with the structure given above, yet the magnitude of the molecular refraction is virtually identical with that calculated for a compound with two double linkings; this exaltation may depend on the relation of the trimethylene ring to the grouping $:CMe_2$, such relation possibly resembling that between two conjugated double linkings.

Oxidation of 1 : 1-dimethyl-2-*iso*butenyl*cyclo*propane by means of 1% potassium permanganate solution proceeds according to the scheme:

$$CH_2{<}\begin{matrix}CMe_2\\ CH{\cdot}CH{:}CMe_2\end{matrix} \longrightarrow CH_2{<}\begin{matrix}CMe_2\\ CH{\cdot}CH(OH){\cdot}CMe_2{\cdot}OH\end{matrix} \longrightarrow$$

$$CH_2{<}\begin{matrix}CMe_2\\ CH{\cdot}CO{\cdot}CMe_2{\cdot}OH\end{matrix} \longrightarrow CH_2{<}\begin{matrix}CMe_2\\ CH{\cdot}CO_2H\end{matrix} + CH_3{\cdot}COMe;$$

the intermediate glycol was not isolated.

The *ketol*, $CH_2{<}\begin{matrix}CMe_2\\ CH{\cdot}CO{\cdot}CMe_2{\cdot}OH\end{matrix}$, is a viscous liquid with an odour resembling terpineol, b. p. 200°/758 mm., $D_0^{16\cdot5}$ 0·9377, D_0^{20} 0·9347, n_D 1·4500, n_D^{20} 1·4490; it exhibits an optical exaltation of 1·43, although that due to the trimethylene ring is usually less than 1. Its *semicarbazone*, $C_9H_{16}O{:}N_2H{\cdot}CO{\cdot}NH_2$, m. p. 127°, and its *phenylurethane*, $C_9H_{15}O{\cdot}O{\cdot}CO{\cdot}NHPh$, crystallise in needles.

1 : 1-*Dimethyl*cyclo*propane-2-carboxylic acid*, $CH_2{<}\begin{matrix}CMe_2\\ CH{\cdot}CO_2H\end{matrix}$, is an oily liquid, b. p. 198°/751 mm., D_0^{18} 0·8990, n_D 1·4385, optical exaltation 0·83; it is stable towards alkaline permanganate solution.

Reduction of 1 : 1-dimethyl-2-*iso*butenyl*cyclo*propane by the method of Sabatier and Senderens, either at 120—125° or at 170°, yields a mixture of (1) a *cyclo*propane derivative, probably 1 : 1-dimethyl-2-*iso*butyl*cyclo*propane, and (2) *ββε-trimethylhexane*,

$$CMe_3\cdot CH_2\cdot CH_2\cdot CHMe_2,$$

b. p. 124—125°/763 mm., D_0^{20} 0·7082—0·7086, n_D 1·3987—1·3998. Treatment of the 1 : 1-dimethyl-2-*iso*butyl*cyclo*propane with hydrogen bromide and subsequently with 2% potassium hydroxide solution yields *βγε-trimethylhexan-β ol*, $OH\cdot CMe_2\cdot CHMe\cdot CH_2\cdot CHMe_2$, b. p. 171—172°/755 mm., D_0^{20} 0·8316, n_D 1·4313.

1 : 1-Dimethyl-2-*iso*butenyl*cyclo*propane combines rapidly with 1 mol. of hydrogen bromide, giving the *monobromo*-derivative,

$$CH_2<\substack{CMe_2\\ |\\ CH\cdot CH_2\cdot CMe_2Br} \text{ or } CH_2<\substack{CMe_2\\ |\\ CH\cdot CHBr\cdot CHMe_2},$$

b. p. 94—96°/31 mm., D_0^{20} 1·1046, whilst the prolonged action of hydrogen bromide yields *δζ-dibromo-βζ-dimethylheptane*,

$$CHMe_2\cdot CH_2\cdot CHBr\cdot CH_2\cdot CMe_2Br,$$

b. p. 134—136°/31 mm., D_0^{20} 1·3846. When distilled with aniline, both the mono- and dibromo-compounds yield *βζ-dimethyl-$\Delta^{\beta\delta}$-heptadiene*, $CMe_2{:}CH\cdot CH{:}CH\cdot CHMe_2$, which contains a small admixture of another hydrocarbon with different positions of the double linkings and has the following approximate physical constants: b. p. 139—141°/758 mm., D_0^{20} 0·7482—0·7510, n_D 1·4456—1·4470. Reduction of this hydrocarbon by Sabatier and Senderens' method at 170° results in the formation of *βζ*-dimethylheptane. T. H. P.

Decomposition of Pyrazoline Bases. Conversion of Cinnamaldehyde into Phenyl*cyclo*propane. NICOLAI M. KISHNER (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 949—957).—*Phenyl*cyclo*propane*,

$CHPh<\substack{CH_2\\ |\\ CH_2}$, prepared by distilling phenylpyrazoline (from cinnamaldehyde and hydrazine) in presence of potassium hydroxide and platinised porous tile, is a liquid, b. p. 173·6°/758 mm., D_0^{15} 0·9449, D_0^{20} 0·9401, n_D^{15} 1·5342. Under the influence of moderately dilute sulphuric acid, it is converted into the same dimeride, $C_{18}H_{20}$, of α-phenyl-Δ^{α}-propylene as is obtained by boiling the latter with sodium.

Phenyl*cyclo*propane combines slowly with hydrogen bromide, yielding *α-bromopropylbenzene*, $CHPhBr\cdot CH_2Me$, b. p. 129—130°/43 mm., D_0^{16} 1·3124, n_D 1·5528. When boiled with aqueous potassium hydroxide, the latter gives (1) the hydrocarbon, $C_{18}H_{20}$, referred to above; (2) phenylethylcarbinol, and (3) allylbenzene, which is also obtained when α-bromopropylbenzene is distilled in presence of quinoline.

In acetic acid solution, the action of bromine on phenyl*cyclo*propane results mainly in the replacement of the nuclear hydrogen, combination of bromine with the trimethylene ring occurring to a very limited extent:

$$CHPh<\substack{CH_2\\ |\\ CH_2} + Br_2 \longrightarrow C_6H_4Br\cdot CH<\substack{CH_2\\ |\\ CH_2} + HBr \longrightarrow C_6H_4Br\cdot CHEtBr.$$

The last compound readily loses hydrogen bromide, giving the unsaturated bromo-derivative, $C_6H_4Br\cdot CH{:}CHMe$, which yields p-bromobenzoic acid on oxidation.

αγ-Dibromopropylbenzene, $CHPhBr\cdot CH_2\cdot CH_2Br$ (?), formed in small proportion in the action of bromine on *cyclo*propane in acetic acid solution, crystallises in prisms, m. p. 125°.

4-Bromo-1-allylbenzene, $C_6H_4Br\cdot CH{:}CHMe$, is a liquid, b. p. 240—241°/764 mm., 124°/20 mm., D_0^{18} 1·3147, n_D 1·5692; owing to the conjugated nature of the double linkings in the ring and the side-chain, it exhibits optical exaltation. On reduction by means of hydriodic acid in a sealed tube, it yields propylbenzene. T. H. P.

Decomposition of Pyrazoline Bases: Synthesis of 1-Methyl-2-isopropyl*cyclo*propane. NICOLAI M. KISHNER (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 987—992).—iso*Butylideneacetone* [*β-Methyl-Δγ-hexylene-ε-one*], $CHMe_2\cdot CH{:}CH\cdot COMe$, prepared by the condensation of isobutyraldehyde and acetone in presence of sodium hydroxide, is a liquid, b. p. 156°/757 mm., D_0^{18} 0·8484, $n_D^{18·5}$ 1·4394; its *semicarbazone*, $C_7H_{12}N\cdot NH\cdot CO\cdot NH_2$, forms hexagonal plates, m. p. 162—163°.

3-Methyl-5-isopropylpyrazoline, $NH<\begin{matrix}CHPr^{\beta}\cdot CH_2\\ | \\ N\!=\!=\!=\!=\!CMe\end{matrix}$, prepared by the action of hydrazine hydrate on *iso*butylideneacetone, is a liquid, b. p. 188·5—189·5°/754 mm., D_0^{17} 0·9081, n_D 1·4640; it oxidises readily in the air, its hot vapours igniting. Its *thioureide*, $C_7H_{13}N_2\cdot CS\cdot NHPh$, crystallises in needles, m. p. 95—100°.

1-Methyl-2-isopropylcyclopropane, $CH_2<\begin{matrix}CHMe\\ | \\ CHPr^{\beta}\end{matrix}$, prepared by decomposition of the preceding compound in a sealed tube at 230°, is a liquid, b. p. 80—81°/748 mm., D_0^{20} 0·7102, n_D^{20} 1·3927, which is extremely stable towards potassium permanganate, combines slowly with bromine in acetic acid solution, and reacts vigorously with fuming nitric acid with formation of a heavy oil. Reduction of 1-methyl-2-*iso*propyl*cyclo*propane by Sabatier and Senderens' method takes place less readily than that of 1 : 1 : 2-trimethyl*cyclo*propane, but at 170° it seems to yield a mixture of βδ-dimethylpentane and βγ-dimethylpentane. With fuming hydrobromic acid it yields *γ-bromo-βδ-dimethylpentane*, b. p. 158—161°/763 mm., D_0^{20} 1·1585, n_D 1·4548, which gives βδ-dimethylpentane on reduction with hydriodic acid.
T. H. P.

Catalytic Reactions at High Temperatures and Pressures. XXXII. VLADIMIR N. IPATIEV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 994—995. Compare this vol., i, 693, 694).—In presence of nickel oxide, indene unites with hydrogen at 250—260° and 110 atmospheres, yielding *octahydrindene*, $\begin{matrix}CH_2\cdot CH_2\cdot CH\cdot CH_2\\ | \qquad\qquad | \\ CH_2\cdot CH_2\cdot CH\cdot CH_2\end{matrix}>CH_2$, which is a liquid, b. p. 165—166°/767 mm., D^{20} 0·8334, n_D^{20} 1·46287 (compare Padoa and Fabris, A., 1908, i, 255). T. H. P.

Metaquinonoids. OTTO STARK, O. GARBEN, and L. KLEBAHN, (*Ber.*, 1913, **46**, 2542—2544. Compare this vol., i, 362, 849).—It is

found that the hydrocarbon, *m-xylylene*, described earlier decomposes at 303—305°, the lower figure given previously being due to insufficient drying.

The substance in the solid state is in a polymerised condition, but the chloroform solutions give ebullioscopic results agreeing with a depolymerised unimolecular product; the solution in chloroform is, however, much more sensitive than that in benzene. The benzene solutions of the substance obtained in the original preparation exhibit a decided fluorescence, and dye paper and linen, whilst the chloroform solutions of the previously separated substance do not possess these characteristics.

A preliminary examination of the absorption spectra of the two solutions indicated complete analogy with the behaviour of Thiele's tetraphenyl-*p*-xylylene; an absorption of blue and violet light which commenced in the green portion of the spectrum was observed both with the chloroform and the original benzene solutions. D. F. T.

Elimination of Halogen Acids by Phosphoric Oxide. I. HANS LECHER (*Ber.*, 1913, **46**, 2664—2668).—Recent publications by Leuchs and his co-workers (this vol., i, 855, 972), in which mention is made of the catalytic action of compounds of phosphorus on the elimination of hydrogen chloride from certain acid chlorides, have led the author to publish a preliminary account of the use of phosphoric oxide in this direction.

Benzoyl chloride does not react with an excess of naphthalene at 180—200°. If, however, a small quantity of phosphoric oxide is added, a vigorous evolution of hydrogen chloride occurs, at the conclusion of which a mixture of much α- and less phenyl β-naphthyl ketone can be isolated, the total amount being 90% of that theoretically possible. Phosphoric oxide has the advantage over aluminium chloride that only small quantities of it are necessary, larger amounts having an unfavourable influence on the course of the reaction. On the other hand, the requisite temperature is high, and, in those cases in which the b. p. of the mixture lies below this temperature, the operation must be performed in sealed tubes. In these circumstances, the liberated hydrogen chloride can only be removed periodically, and greatly diminishes the velocity of the reaction. Thus, only small yields of benzophenone could be obtained by this method from benzoyl chloride and benzene.

Boiling benzyl chloride rapidly and completely eliminates hydrogen chloride in the presence of phosphoric oxide, forming a mixture of hydrocarbons which has not yet been completely investigated. ω-Chlorotriphenylmethane is similarly decomposed at about 150° into 9-phenylfluorene and much triphenylmethane.

A series of experiments has been performed to determine the exact nature of the catalyst. Bailey and Fowler (T., 1888, **53**, 755) have shown that phosphoric oxide reacts with hydrogen chloride according to the equation: $P_4O_{10} + 3HCl = POCl_3 + 3HPO_3$, but the author finds that no appreciable action occurs within a reasonable time at temperatures up to 260°, and, hence, that phosphoryl chloride cannot

be the actual catalyst. Direct experiment with metaphosphoric acid has shown that this substance is also inactive.

Finally, the active catalyst can easily be recovered by the removal of organic matter by extraction with benzene. In this manner, a mixture of a phosphorus compound (which yields metaphosphoric acid with water) and small quantities of carbon is obtained, which can be employed in the same manner as fresh phosphorus pentoxide.

H. W.

Morphological Studies in the Benzene Series. IV. The Crystalline Form of Sulphonates in Relation to their Molecular Structure. ERNEST H. RODD (*Proc. Roy. Soc.*, 1913, A, 89, 292—313. Compare T., 1910, **97**, 1578; A., 1912, i, 756).—A number of salts of *p*-dichlorobenzonosulphonic acid have been prepared, and their crystallographic constants have been compared. Lanthanum *p*-dichlorosulphonate, $La(C_6H_3Cl_2SO_3)_3,15H_2O$, is deposited from solution between 10° and 50°; it forms triclinic prisms, which rapidly effloresce [$a:b:c = 1·6193:1:1·6028$; $\alpha = 76°26'$; $\beta = 113°48'$; $\gamma = 63°6'$]. Neodymium *p*-dichlorobenzenesulphonate,

$$Nd(C_6H_3Cl_2SO_3)_3,12H_2O,$$

crystallises in short, thick, rose-coloured, monoclinic prisms between 15° and 50°, closely isomorphous with $Gd(C_6H_3Br_2SO_3)_3,12H_2O$ [$a:b:c=0·5872:1:0·3810$; $\beta=76°34'$]. Praseodymium *p*-dichlorobenzenesulphonate, $Pr(C_6H_3Cl_2SO_3)_3,12H_2O$, forms pale green, monoclinic prisms isomorphous with the corresponding neodymium salt [$a:b:c=0·5887:1:0·3819$: $\beta=76°26'$]. A salt of the composition $Pr(C_6H_3Cl_2SO_3)_3,15H_2O$, isomorphous with the corresponding lanthanum salt, is formed when a supersaturated solution is allowed to spontaneously crystallise at the ordinary temperature. A number of other sulphonates have also been prepared and measured. Gadolinium *p*-dibromobenzene sulphonate, $Gd(C_6H_3Br_2SO_3)_3,7H_2O$, monoclinic prisms [$a:b:c=1·2595:1:0·6031$; $\beta=89°16'$]. Didymium benzenesulphonate, $Di(C_6H_5·SO_3)_3,9H_2O$, crystallises from a mixture of aqueous alcohol and ethyl acetate in thin, hexagonal-shaped plates belonging to the rhombic system [$a:b:c=2·0795:1:1·9374$]. Potassium *p*-dichlorobenzenesulphonate, $C_6H_3Cl_2SO_3K$, crystallises anhydrous from aqueous solutions between 20° and 37° in thin, monoclinic prisms [$a:b:c=1·5054:1:0·7636$; $\beta=83°27·5'$]. Sodium *p*-dichlorobenzenesulphonate, $C_6H_3Cl_2SO_3Na,H_2O$, crystallises in large, monoclinic tablets at 37° [$a:b:c=3·0529:1:1·9583$; $\beta=88°46'$]. Zinc *p*-dichlorobenzenesulphonate, $Zn(C_6H_3Cl_2SO_3)_2,8H_2O$, forms long, monoclinic prisms, which are always distorted [$a:b:c=2·9985:1:2·4539$; $\beta=79°20'$]. Magnesium *p*-dichlorobenzenesulphonate,

$$Mg(C_6H_3Cl_2SO_3)_2,8H_2O,$$

crystallises in stout, monoclinic, hemimorphic plates [$a:b:c=2·9970:1:2·4450$; $\beta=79°41·5'$]. Ferric *p*-dibromobenzenesulphonate, $Fe(C_6H_3Br_2SO_3)_3,13H_2O$; basic ferric *p*-dibromobenzenesulphonate, $Fe(OH)(C_6H_3Br_2SO_3)_2,12H_2O$; chromium *p*-dibromobenzenesulphonate, $Cr(C_6H_3Br_2SO_3)_3,14H_2O$; aluminium *p*-dibromobenzenesulphonate,

$$Al(C_6H_3Br_2SO_3)_3,18H_2O;$$

scandium *p*-dibromobenzenesulphonate, $Sc(C_6H_3Br_2SO_3)_3,14H_2O$, and

cobaltous *p*-dibromobenzenesulphonate, $Co(C_6H_3Br_2SO_3)_2,9H_2O$, have been prepared and described without crystallographic details. It is shown that similar conclusions may be drawn with regard to the structure of *p*-dichlorosulphonic acid as were drawn in the case of *p*-dibromosulphonic acid in the previous paper (*loc. cit.*). The structure of the sulphonates of monad and dyad metals is discussed; it is argued that in the formation of the latter the molecules of benzene in contiguous rows become separated by the intervention of the sulphonic radicles which are united in pairs by the metallic atom. The structure of the salts containing monad metals appears in some cases to be pseudo-trigonal like that of the acid; in others to resemble that of the dyad metals. J. F. S.

***p*- and *o*-Toluenesulphinic Acids.** ALFRED HEIDUSCHKA and HANS LANGKAMMERER (*J. pr. Chem.*, 1913, [ii], **88**, 425—442).—An extension of the work of E. von Meyer and others (A., 1901, i, 264; 1903, i, 808) on the formation of aminodiaryl sulphides by the interaction of aromatic sulphinic acids and amines.

The authors find that the sulphides are obtained in a purer condition and better yield by fusing the sulphinic acids with the hydrochlorides of the amines, instead of with the free bases.

When *p*-toluenesulphinic acid is fused at 215° with aniline hydrochloride and the product extracted with ether, p-*aminophenyl* p-*tolyl sulphide* p-*toluenesulphonate*, $C_{20}H_{21}O_3NS_2$, is obtained in white needles, m. p. 216°; extraction of the residue with hydrochloric acid yields the corresponding *hydrochloride*.

p-Aminophenyl *p*-tolyl sulphide condenses with 4-bromo-2-hydroxybenzaldehyde in boiling alcoholic solution to form p-4-*bromo-2-hydroxybenzylideneaminophenyl* p-*tolyl sulphide*,

$$C_6H_4Me \cdot S \cdot C_6H_4 \cdot N:CH \cdot C_6H_3Br \cdot OH,$$

which crystallises in lustrous, brownish-yellow leaflets, m. p. 148°; the m-*xylylidene* derivative, $C_6H_4(CH:N \cdot C_6H_4 \cdot S \cdot C_6H_4Me)_2$, from *m*-phthalaldehyde, has m. p. 163°.

The *benzylidene* derivative, $C_6H_4Me \cdot S \cdot C_6H_4 \cdot N:CHPh$, is obtained in the form of its *hydrochloride* (yellow needles, m. p. 164°, which rapidly acquire a greenish colour) by condensing benzaldehyde with *p*-aminophenyl *p*-tolyl sulphide hydrochloride; the *hydrochlorides* of the *salicylidene* and *vanillylidene* derivatives have m. p. 175° and 195° respectively.

The aqueous extract of the product obtained by fusing *o*-anisidine hydrochloride with *p*-toluenesulphinic acid at 225° yields o-*anisidine* p-*toluenesulphonate*, $C_{14}H_{17}O_4NS$, which has m. p. 150°, and has also been prepared directly from its components in alcoholic solution; extraction of the product with hydrochloric acid yields 4-*amino-3-methoxyphenyl* p-*tolyl sulphide hydrochloride*,

$$C_6H_4Me \cdot S \cdot C_6H_3(OMe) \cdot NH_2,HCl.$$

This has m. p. 215°, and on treatment with aqueous ammonia yields the free *base*, which, however, could not be obtained in a pure condition. The free base combines with phenylcarbimide in ethereal solution to form the *carbamide*, m. p. 163°,

$$NHPh \cdot CO \cdot NH \cdot C_6H_3(OMe) \cdot S \cdot C_6H_4Me.$$

o-*Anisidine* p-*toluenesulphinate*, prepared from its components in alcoholic solution, has m. p. 112°. o-*Chloroaniline* p-*toluenesulphonate*, m. p. 198°, and o-*chloroaniline* p-*toluenesulphinate*, m. p. 150°, were prepared in a similar manner.

3-Chloro-4-aminophenyl p-*tolyl sulphide hydrochloride*,

$$C_6H_4Me\cdot S\cdot C_6H_3Cl\cdot NH_2,HCl,$$

obtained by fusing *p*-toluenesulphinic acid with *o*-chloroaniline hydrochloride, forms colourless crystals, m. p. 150°, and on treatment with aqueous ammonia yields the free *base*, which combines with phenylcarbimide in ethereal solution to form the *carbamide*,

$$NHPh\cdot CO\cdot NH\cdot C_6H_3Cl\cdot S\cdot C_6H_4Me,$$

crystallising in white needles, m. p. 190°; the corresponding *thiocarbamide* prepared in a similar manner has m. p. 147°.

p-*Aminophenyl* o-*tolyl sulphide*, $NH_2\cdot C_6H_4\cdot S\cdot C_6H_4Me$, obtained in the form of its o-*toluenesulphonate*, $C_{20}H_{21}O_3NS_2$, m. p. 190°, by fusing aniline hydrochloride with *o*-toluenesulphinic acid and extracting the product with water, separates from ether in flat, hexagonal, brown pyramids, m. p. 50°, forms a *hydrochloride*, crystallising in slender, white needles, m. p. 137°, and condenses with benzaldehyde in alcoholic solution, yielding the *benzylidene* derivative, which was isolated in the form of its *hydrochloride*, $C_6H_4Me\cdot S\cdot C_6H_4\cdot N\!:\!CHPh,HCl$, as a yellow powder, m. p. 195°. It combines with phenylcarbimide in ethereal solution yielding the *carbamide*, $NHPh\cdot CO\cdot NH\cdot C_6H_4\cdot S\cdot C_6H_4Me$, crystallising in white needles, m. p. 164°. F. B.

Electrochemical Reduction of Organic Halogen Compounds. II. KURT BRAND (*Ber.*, 1913, **46**, 2935—2942).—This and the succeeding paper give the results of attempts to reproduce by electrochemical methods the conversion of diaryltrichloroethanes into stilbene derivatives, first effected by chemical methods by Goldschmidt, and later by Elbs (Abstr., 1893, i, 271). The results show that the products obtained depend in part on the nature of the cathode used. The apparatus used is described. The cathode liquid, which was kept boiling, consisted of the substance under examination in alcohol and hydrochloric acid.

Lead cathode.—βββ-Trichloro-αα-diphenylethane yielded stilbene (4% of the theoretical) and dichlorodiphenylethane. βββ-Trichloro-αα-di-*p*-tolylethane gave 6% of the theoretical yield of *p*:*p*′-dimethylstilbene. βββ-Trichloro-αα-di-*p*-anisylethane gave about 10% of the calculated yield of *p*:*p*′-dimethoxystilbene, and a similar yield of *p*:*p*′-diethoxystilbene was obtained from βββ-trichloro-αα-di-*p*-phenetylethane. These alkylstilbenes were identified by means of their dibromides.

Copper cathode.—The four diaryltrichloroethanes mentioned in the preceding paragraph were also submitted to electrolytic reduction in presence of a copper cathode, and then yielded the corresponding diaryldichloroethanes, but the first-named product gave only a small yield. The last-named substance also yielded a minute amount of the corresponding diethoxystilbene. The diaryldichloroethanes were identified by conversion into the corresponding ethylenes, which give characteristic colours with sulphuric acid. T. A. H.

Electrochemical Reduction of Organic Halogen Compounds. III. KURT BRAND and M. MATSUI (*Ber.*, 1913, **46**, 2942–2951).—It has been shown previously (Brand, *Zeitsch. Elektrochem.*, 1910, **16**, 669) that the principal product of the electrolytic reduction of hot alcoholic solutions of $\beta\beta\beta$-trichloro-$\alpha\alpha$-diphenylethane in presence of a lead cathode is a hydrocarbon, $C_{28}H_{22}$, which may have the constitution $CHPh_2\cdot C\vdots C\cdot CHPh_2$ or $CPh_2\colon C\colon CH\cdot CHPh_2$ (see also preceding abstract). It is now shown that the cathodic reduction of $\beta\beta\beta$-trichloro-$\alpha\alpha$-di-*p*-tolylethane and of di-$\beta\beta\beta$-trichloro-$\alpha\alpha$-di-*p*-anisylethane under analogous conditions furnishes similar substances, some reactions of which are described. These reactions do not enable a final decision as to the constitution to be arrived at, but on the whole they tend to support formulæ of the kind represented by the second given above.

$\beta\beta\beta$-Trichloro-$\alpha\alpha$-di-*p*-tolylethane furnishes the *hydrocarbon*, $C_{32}H_{30}$, m. p. 123°, which crystallises from boiling alcohol in colourless, small needles, shows a faint blue fluorescence, and on oxidation in acetone solution with potassium permanganate yields di-*p*-tolylacetic acid and di-*p*-tolyl ketone; the same products are formed with calcium permanganate in presence of pyridine, and with chromic acid in acetic acid, but in different amounts. On reduction with excess of sodium in amyl alcohol, the hydrocarbon yields the corresponding *tetra*-p-*tolylbutane*, m. p. 126°, crystallising from alcohol in colourless needles showing a slight blue fluorescence. With insufficient sodium, a *substance*, m. p. 186°, crystallising in glancing leaflets, is formed in small quantity. With sodium in absolute alcohol, the same reduction takes place. On treatment with sodium ethoxide in alcohol, the hydrocarbon is converted into $\alpha\alpha\delta\delta$-*tetra*-p-*tolyl*-$\Delta^{\alpha\gamma}$-*butadiene*,

$$C(C_6H_4Me)_2\colon CH\cdot CH\colon C(C_6H_4Me)_2,$$

m. p. 255°, which crystallises from methyl ethyl ketone in heavy, green, fluorescent needles, is sparingly soluble in boiling alcohol, but readily so in chloroform or benzene, giving solutions which are green in colour and show absorption in the extreme violet end of the spectrum. The hydrocarbon, $C_{32}H_{30}$, reacts with mercuric acetate to form an orange-yellow *compound* of uncertain composition, which with hydrogen chloride or with zinc and acetic acid yields the tetratolylbutadiene described above.

Di-*p*-anisyltrichloroethane yields in addition to di-*p*-methoxystilbene (preceding abstract) the *phenol ether*, $C_{32}H_{30}O_4$, which, as indicated above, is probably $\alpha\alpha\delta\delta$-tetra-*p*-anisyl-$\Delta^{\alpha\beta}$-butadiene,

$$(C_6H_4\cdot OMe)_2C\colon C\colon CH\cdot CH(C_6H_4\cdot OMe)_2.$$

It melts at 111°, crystallises from boiling alcohol in colourless needles, and on oxidation with chromic acid gives di-*p*-anisyl ketone and a small amount of di-*p*-anisylacetic acid. On reduction with sodium in amyl alcohol, $\alpha\alpha\delta\delta$-*tetra*-p-*anisylbutane*, m. p. 116°, crystallising in colourless needles with a blue fluorescence, is formed, whilst with sodium ethoxide in alcohol, $\alpha\alpha\delta\delta$-*tetra*-p-*anisyl*-$\Delta^{\alpha\gamma}$-*butadiene*, m. p. 149°, which crystallises from methyl ethyl ketone in green, fluorescent needles, is produced. These two substances closely resemble their analogues described in the preceding paragraph.

T. A. H.

Dehydrobenzylidenebisfluorene. ROBERT STOLLÉ (*Ber.*, 1913, 46, 2979).—In preparing benzylfluorene by Werner's method (A., 1906, i, 436), but using potassium ethoxide instead of sodium, the author has obtained a small quantity of *dehydrobenzylidenebisfluorene*, $C_{27}H_{16}$, m. p. 350°, which crystallises from chloroform in small, orange needles, and on heating sublimes to form red crystals. It is hardly soluble in ether or alcohol, and sparingly soluble in hot benzene or acetic acid. The analogous ethylidene compound has been described by Pummerer and Dorfmüller (this vol., i, 963). T. A. H.

Studies in the Fluorene Series. FRITZ MAYER (*Ber.*, 1913, 46, 2579—2587).—The author has attempted to synthesise fluoranthene by the ring condensation of 9-ethylfluorene, fluorene-9-acetic acid or fluorenepropionic acid, but without success. On heating distilled ethylfluorene with litharge and distilling the product, 9-ethylidene-fluorene, $\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}\!>\!C{:}CHMe$ (Ullmann, A., 1906, i, 77), which formed a picrate, m. p. 156°, was obtained. When crude ethylfluorene was employed, however, and the product was not distilled, a 9-fluorene-ethyl alcohol, which also gave a picrate, m. p. 155—156°, was formed. It was not identical with Ullmann's carbinol (*ibid.*) and has therefore the constitution $\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}\!>\!CH\cdot CH(OH)Me$ or $\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}\!>\!CH\cdot CH_2\cdot CH_2\cdot OH$. In each case, very small quantities of high-melting, red hydrocarbons of the formula $C_{15}H_{10}$ were obtained. It was expected that one of them would be identical with the compound,

$$\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}\!>\!CH\cdot CH{:}C\!<\!\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4},$$

described by Wislicenus and Densch (A., 1902, i, 291), but the author could not prepare this substance by any means.

Twenty grams of crude 9-ethylfluorene, from the action of ethyl iodide on ethyl fluorene-9-oxalate (*loc. cit.*), were heated for fifteen minutes at 310—360° with 40 grams of litharge, when the product was extracted with boiling chloroform. The solvent deposited a red *hydrocarbon*, $C_{15}H_{10}$ or $C_{27}H_{18}$, m. p. over 360°, on cooling, and the dark brown *picrate* of a fluorene-ethyl alcohol, $C_{21}H_{17}O_8N_3$, m. p. 155—156°, was obtained from the mother liquor. The *picrate* of Ullmann's carbinol has the same m. p., but not so a mixture of the two.

Two parts of distilled 9-ethylfluorene, b. p. 306—310°, were heated with five parts of litharge for one hour, the product was extracted with hot chloroform, which deposited a red *hydrocarbon*, $(C_{15}H_{10})_x$, m. p. 300—310°, and the residue, after evaporating the solvent, was distilled. The fraction, b. p. 310—320°, contained ethylidenefluorene and formed a *picrate*, $C_{21}H_{15}O_7N_3$, m. p. 155—156°.

For the preparation of *fluorene-9-acetic acid*, $\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}\!>\!CH\cdot CH_2\cdot CO_2H$, ethyl fluorene-9-oxalate was treated with sodium in alcohol and ethyl bromoacetate, and the product was hydrolysed by 20% aqueous sodium hydroxide. The acid has m. p. 129—130°, forms a *methyl* ester,

$C_{16}H_{14}O_2$, m. p. 60°, an *amide*, $C_{15}H_{13}ON$, slender needles, m. p. 189°, and yields 9-methylfluorene (*ibid.*) on distillation with soda-lime. *Fluorene-9-propionic acid*, $C_{16}H_{14}O_2$, was also prepared, using ethyl β-iodopropionate; it forms white needles, m. p. 144°. Neither the acids themselves nor their chlorides gave definite products on condensation. J. C. W.

Tri-β-naphthylmethane and Certain of its Derivatives. ALEXEI E. TSCHITSCHIBABIN and S. I. KORJAGIN (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 766—781; *J. pr. Chem*, 1913, [ii], **88**, 505—578).—Tri-β-naphthylcarbinol (compare Schmidlin and Huber, A., 1910, i, 832) may be readily obtained by the interaction of di-β-naphthyl ketone and magnesium β-naphthyl bromide (see A., 1911, i, 969) in presence of ether.

The authors were unable to prepare 2-bromonaphthalene by Darzens and Berger's method (A., 1909, i, 297), but obtained it readily from β-naphthylamine by passing through the diazo-compound.

Di-β-naphthyl ketone (compare Grucarevic and Merz, A., 1873, 263, 264) was prepared by the dry distillation of calcium β-naphthoate, by oxidising di-β-naphthylcarbinol by the action of β-naphthoyl chloride on naphthalene in presence of zinc and by the action of magnesium β-naphthyl bromide on β-naphthoyl chloride. The first method gives poor, and the last good yields.

Tri-β-naphthylcarbinol, $C_{31}H_{22}O$, forms snow-white crystals, m. p. 204°, and dissolves in concentrated sulphuric acid with an intense coloration, which is greenish in thin layers or low concentrations, and violet-red when more concentrated. These solutions show an absorption band gradually weakening from the violet to the blue, with a maximum intensity at about 490 μμ, and also a faint band in the red, beginning at about 755 μμ. Unlike the isomeric tri-α-naphthylcarbinol (A., 1911, i, 969), it shows no inclination to oxidise in the air. *Tri-β-naphthylchloromethane*, $C_{31}H_{21}Cl$, forms white crystals, m. p. 199—201° (decomp.), the fused mass solidifying later, and then showing m. p. 231—236°; with sulphuric acid it gives the same coloration as the carbinol.

Tri-β-naphthylmethane, $C_{31}H_{22}$, prepared by reducing the above carbinol or chloride by means of hydriodic and glacial acetic acids (A., 1911, i, 277), forms colourless, prismatic crystals, m. p. 178—179°, and exhibits the normal molecular weight in freezing benzene. When crystallised from benzene, it yields crystals containing varying proportions of benzene, possibly owing to the formation of a solid solution.

β-Naphthyldi-ββ-naphthafluorene, $C_{31}H_{20}$, obtained on reduction of the impure tri-β-naphthylchloromethane or by heating the latter above its melting point in an atmosphere of carbon dioxide, forms white, nodular crystals, which melt at 235—237° in a sealed capillary filled with carbon dioxide. Its solutions exhibit intense blue fluorescence and react with magnesium methyl iodide with evolution of methane.

The action of copper-bronze or of Gomberg and Cone's molecular silver (A., 1906, i, 822) on a solution of tri-β-naphthyl-

chloromethane yields a dark violet-red liquid from which dark violet crystals were separated. These have not been analysed, but from their colour and ready oxidisability in the air, and the molecular weights indicated by cryoscopic measurements in benzene and naphthalene, it seems probable that they consist principally of *tri β-naphthylmethyl*, $C(C_{10}H_7)_3$, and to a small extent of hexa-β-naphthylethane. T. H. P.

Phenyldichloroamine [Di-ω-chloroaniline]. STEFAN GOLDSCHMIDT (*Ber.*, 1913, **46**, 2728—2736).—The existence of di-ω-chloroaniline and ω-chloroaniline as intermediate products in the action of hypochlorites on aniline has already been indicated by Raschig (*Zeitsch. angew. Chem.*, 1907, **20**, 2065; compare also Bamberger, A., 1894, i, 238).

The dichloro-compound has now been isolated by the author by the interaction of aniline and hypochlorous acid in ethereal solution at a low temperature. The ethereal solution of hypochlorous acid is obtained by extracting an aqueous solution of the acid, prepared according to Wohl's method (A., 1907, i, 194), with ether, and rapidly cooling to $-15°$. At the ordinary temperature the solution is unstable and rapidly decomposes, yielding acetaldehyde and hydrogen chloride.

When treated with slightly less than the calculated amount of aniline in ethereal solution at $-15°$ to $-20°$, a yellow solution is obtained, which on evaporation at $-40°$ yields *di-ω-chloroaniline*, $NPhCl_2$, as a viscid oil, having a colour similar to that of potassium dichromate. Although in the free condition, the dichloroamine is very unstable and decomposes explosively when removed from the freezing mixture; in ethereal solution it may be kept for several hours without undergoing appreciable change. It liberates iodine from potassium iodide, and on treatment with ethereal hydrogen chloride rapidly decomposes, with the formation of 2:4-dichloroaniline and 2:4:6-trichloroaniline.

When treated with sodium hydroxide, alcoholic ammonia, sodium thiosulphate, aniline or copper powder, it yields *p*-aminodiphenylamine hydrazobenzene and benzoquinonephenyldi-imine; it is probable that the free radicle NPh: is formed as an intermediate product in these decompositions.

Attempts to prepare ω-chloroaniline by the interaction of molecular quantities of aniline and hypochlorous acid in ethereal solution at a low temperature were unsuccessful.

ωω-2:4:6-Pentachloroaniline, prepared from 2:4:6-trichloroaniline and hypochlorous acid in a similar manner to that described above for the preparation of di-ω-chloroaniline, is much more stable than the latter compound, and forms a viscid oil having the colour of diphenylketen. It has a sweet, disagreeable odour resembling that of chlorine, and solidifies at $-80°$ to a glassy mass. When heated, it becomes dark in colour and decomposes explosively with the production of flame. It dissolves in strong sulphuric acid, yielding violet solutions, which become yellow and evolve chlorine, when warmed.

On the addition of potassium iodide in aqueous alcoholic solution to an ethereal solution of the dichloro-compound, iodine (2 atoms) is liberated and 2 : 4 : 6 : 2′ : 4′ : 6′-hexachloroazobenzene is formed; in the presence of hydrochloric acid, 2 : 4 : 6-trichloroaniline is produced, the amount of iodine liberated in this case being twice that given above.

A sketch of the apparatus employed in the preparation of the dichloroamines is given. F. B.

A New Group of Metallic Compounds of the Aromatic Thiocarbamide Series. RUDOLF KRULLA (*Ber.*, 1913, 46, 2669—2672).—Aryl thiocarbamides are readily prepared by the action of aryl amines on carbon disulphide in the presence of a substance which absorbs the liberated hydrogen sulphide. For this purpose, the author recommends nitrobenzene, which reacts in accordance with the equation: $5NH_2Ph + 3CS_2 + Ph{\cdot}NO_2 = 3(PhNH)_2CS + 2H_2O + 3S$. He has also employed a number of metallic oxides and salts for this purpose, and thus obtained a new series of organometallic derivatives, of which the *tin* compounds have been most completely investigated.

When an alcoholic solution of aniline and carbon disulphide is treated with tin hydroxide, a yellow tin salt, $Sn(S{\cdot}CS{\cdot}NHPh)_2$, is immediately precipitated in a practically pure condition. Like the similar salts of other metals, it is almost insoluble in most solvents except acetone and a mixture of acetone and alcohol, and is readily decomposed when warmed, even in solution. Warm acids immediately convert it into diphenylthiocarbamide and the corresponding metallic salt, whilst prolonged contact with aniline causes a similar change. Lead hydroxide similarly yields a *lead* salt, fine needles, when added to a dilute alcoholic solution of aniline and carbon disulphide; in concentrated solution, however, a dark green coloration is observed, and hydrogen sulphide is evolved with perceptible heat evolution. This appears to be the only case in which hydrogen sulphide is given off.

The *bismuth* salt forms long needles, readily soluble in alcohol.

In the cases of arsenic and antimony, the organometallic derivatives could not be isolated, the thiocarbamide and the metallic sulphide being the products of the action. Copper behaved similarly to the alkali metals, forming xanthates.

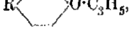
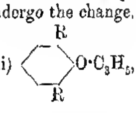
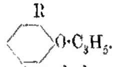
Homologues of aniline which do not contain too many acidic groups react analogously. In these cases it often occurs that lead oxide or hydroxide is active when tin is no longer useful. Organometallic derivatives have been obtained from *p*-toluidine, monomethylaniline, *p*-aminophenol, α- and β-naphthylamine. Diphenylamine did not react. H. W.

New Methods of Preparing Thiocarbanilides. HARRY S. FRY (*J. Amer. Chem. Soc.*, 1913, 35, 1539—1546).—The method of preparing thiocarbanilides by the interaction of carbon disulphide and an aromatic amine frequently fails in its desired object, and the cause is attributed to the alcohol and potassium hydroxide which are generally introduced into the reaction mixture. By omitting the

...and replacing the alkali by pyridine, the process is so improved ... a better yield of a purer product is just as readily obtained. A specimen of di-*o*-chlorophenylthiocarbamide prepared in this manner ... m. p. 130·5° (compare Grosch, A., 1899, i, 599).

By applying iodine together with pyridine, the former to remove the hydrogen sulphide from the primary reaction and the latter to combine with the hydriodic acid formed in the secondary reaction of the hydrogen sulphide, excellent yields of the various thiocarbanilide compounds can be obtained; the process in this respect is greatly superior to the previous one. The reaction may be summed up by the equation: $2NH_2R + CS_2 + I_2 + 2C_5H_5N = CS(NHR)_2 + C_5H_5N,HI + S$. An excess of carbon disulphide is applied (both in this and in the previous method), and during the action which occurs without warming, pyridine hydriodide separates. The reaction product is steam distilled, and the mixture of thiocarbanilide and sulphur obtained by filtration of the aqueous residue is then separated by extraction with alcohol.

In the preparation by the latter process with iodine it is important that only the theoretical proportions of aniline and iodine should be used. With excess of iodine, the reaction proceeds quantitatively to the formation of a thiocarbimide according to the equation: $NH_2R + CS_2 + I_2 + 2C_5H_5N = RNCS + 2C_5H_5N,HI + S$. Indeed, this reaction provides a convenient method for the estimation of aniline (dissolved in a mixture of carbon disulphide and pyridine) by direct titration with a solution of iodine in carbon disulphide. D. F. T.

Transformation of Phenyl Allyl Ethers into the Isomeric Allylphenols. LUDWIG CLAISEN and OTTO EISLEB (*Annalen*, 1913, 401, 21—119).—It has been shown (A., 1912, i, 965) that the allyl ethers of several phenols change almost quantitatively by heating, sometimes even below the b. p., to the isomeric allylphenols. In order to test the generality of the change, a large number of aromatic allyl ethers have been examined; all without exception undergo the change. The ethers are of the types (i) , (ii) , and (iii) . Those of type (i) change very easily to *o*-allylphenols, and those of type (ii) readily to *p*-allylphenols. Ethers of type (iii) yield *o*-allylphenols, so the allyl group preferentially enters the nucleus in the ortho-position to the hydroxyl group. The b. p.'s/10 mm. of the allylphenols and also the densities are generally higher than the corresponding constants of the isomeric allyl ethers; exceptions, however, are the allyl ethers of phenols containing a negative substituent in the ortho-position to the hydroxyl group, the b. p.'s of these being higher than the b. p.'s of the isomeric allylphenols.

With suitable ethers changes such as:

$$p\text{-}OMe\cdot C_6H_4\cdot O\cdot C_3H_5 \longrightarrow OMe\cdot C_6H_3(C_3H_5)\cdot OH \longrightarrow$$
$$OMe\cdot C_6H_3(C_3H_5)\cdot O\cdot C_3H_5 \longrightarrow OMe\cdot C_6H_2(C_3H_5)_2\cdot OH$$

proceed with good yields. Such changes occur particularly easily with allyl ethers of phenolaldehydes and phenolcarboxylic acids and their esters. However, when the aldehyde or carboxyl group occupies a position in the nucleus into which the allyl group desires to enter, it is eliminated as carbon monoxide or carbon dioxide respectively; for example, by alternate heating and allylation, esters of *o*-allyloxybenzoic acid are converted into 2-allyloxy-3 : 5-diallylbenzoates; the latter then change to 2 : 4 : 6-triallylphenol by hydrolysis and heating.

In addition to the change to *o*-propenylphenols by heating with aqueous potassium hydroxide (*loc. cit.*), *o*-allylphenols are changed in another manner by heating with an acid catalyst, such as pyridine hydrochloride; this change, whereby dihydrocoumarones are produced, $OH\cdot C_6H_4\cdot CH_2\cdot CH:CH_2 \longrightarrow C_6H_4<\overset{CH_2}{\underset{O}{}}>CHMe$, will be described in a future communication.

The aromatic allyl ethers described below are prepared generally by boiling the phenol in acetone with allyl bromide and finely powdered potassium carbonate. For the preparation of the allyl bromide, Merling and Jacobi's hydrogen bromide method (A., 1894, i, 162) is recommended, the yield being 85%. An apparatus is figured and described by which 120—150 grams of hydrogen bromide per hour can be obtained quantitatively from its elements.

Although the change frequently occurs at lower temperatures, the optimum temperature, at which the change is complete usually in a few seconds or minutes, for the conversion of the aromatic allyl ether into the allylphenol is 230—250°. Difficultly volatile phenyl allyl ethers cannot have a b. p. under ordinary pressures, because they change to the allylphenol before the b. p. is reached.

p-*Chlorophenyl allyl ether*, $C_6H_4Cl\cdot OC_3H_5$, b. p. 106—107°/12 mm., D^{15} 1·131, a colourless liquid having an odour of aniseed, is converted by boiling for twenty to twenty-five minutes into 4-*chloro-2-allylphenol*, $OH\cdot C_6H_3Cl\cdot C_3H_5$, m. p. 48°, b. p. 256—260° or 124—125°/12 mm., D^{15} 1·171 (supercooled liquid), which develops an olive-green coloration with alcoholic ferric chloride and forms a p-*nitrobenzoate*, m. p. 82°. p-*Bromophenyl allyl ether*, b. p. 126°/14 mm., yields by boiling for a few minutes 4-*bromo-2-allylphenol*, m. p. 50°, b. p. 274—280° or 142—144°/14 mm. p-*Nitrophenyl allyl ether*, m. p. 18·5°, b. p. 160°/12 mm., faintly yellow prisms, yields about 40% of 4-*nitro-2-allylphenol* at 260°; the latter has m. p. 79°, b. p. 190°/11 mm., and crystallises in colourless leaflets. p-*Benzeneazophenyl allyl ether*,

$$C_6H_5\cdot N_2\cdot C_6H_4\cdot O\cdot C_3H_5,$$

m. p. 52°, yellowish-red needles and prisms, yields by heating in petroleum at 230° about 70% of *o-allylbenzeneazophenol*, m. p. 97—98°, yellow needles and prisms (*benzoate*, m. p. 92°, brownish-red crystals).

p-*Tolyl allyl ether*, b. p. 211—213° or 91°/12 mm., D^{15} 0·967, yields by boiling for one hour 3-*allyl*-p-*cresol*, b. p. 236—238° or 112°/12 mm., D^{15} 1·006 (p-*nitrobenzoate*, m. p. 69°). By heating with potassium hydroxide and water at 140—145°, 3-allyl-*p*-cresol is converted into 3-*propenyl*-p-*cresol*, b. p. 120—124°/11 mm., the *methyl ether* of which is oxidised to 4-methoxy*iso*phthalic acid by potassium permanganate. By allylation, 3-allyl-*p*-cresol yields 3-*allyl*-p-*tolyl allyl ether*, b. p.

123—127°/14 mm., from which is obtained by prolonged heating a very small quantity of a *substance*, h. p. 135—145°/14 mm., which is possibly 1-*methyl*-3 : 5-*diallylphenol*.

Eugenol allyl ether, b. p. 140°/9 mm., D^{15} 1·024, changes very easily at 230° to o-*allyleugenol*, h. p. 285—287° or 149°/10 mm., D^{15} 1·036, which develops a deep blue to deep green coloration with alcoholic ferric chloride and forms a p-*nitrobenzoate*, m. p. 136°.

The eugenol obtained previously (*loc. cit.*) hy the transformation of guaiacyl allyl ether is now definitely proved to be o-eugenol (o-allylguaiacol), since it yields by treatment with aqueous potassium hydroxide at 170° a propenylguaiacol, m. p. 78°, which is identical with Pauly and Battlu's o-*iso*eugenol, (A., 1911, i, 785). o-*Eugenyl allyl ether*, h. p. 128°/10 mm., D^{15} 1·016, changes at 200° to o-allyleugenol, identical with the substance obtained by the transformation of eugenyl allyl ether.

o-*Tolyl allyl ether*, b. p. 205—208° or 85°/12 mm., D^{15} 0·969, is changed by boiling to 2-*methyl*-3-*allylphenol*, h. p. 231—233° or 106—107°/12 mm., D^{15} 1·007, which must contain the allyl group in the ortho-position to the hydroxyl group, since it is also obtained by heating 2-allyloxy-*m*-toluic acid (see helow).

m-*Tolyl allyl ether*, h. p. 211—214° or 92—94°/12 mm., D^{15} 0·965, is changed by boiling to 3-*methyl*-2(or 4)-*allylphenol*, b. p. 239—240° or 111—112°/11 mm., D^{15} 1 012; since the liquid has heen separated into liquid and a solid, m. p. 53°, possibly both allyl-*m*-cresols are present in it. By further allylation it yields *allyl-m-tolyl allyl ether*, which changes at 230° to 3-*methyl*-2 : 4-*diallylphenol*, b. p. 272—274° or 140°/5 mm., to the extent of about 30%.

o-*Nitrophenyl allyl ether*, h. p. 155°/12 mm., is changed hy heating at 8?° for five hours to 6(?)-*allyl*-o-*nitrophenol*, m. p. 9°, h. p. 130—135°/15 mm. (*barium* salt, golden-red leaflets).

a-*Naphthyl allyl ether* is an oil which cannot be distilled, even under diminished pressure, without partly changing to 2-*allyl*-a-*naphthol*, b. p. 171°/12 mm. (p-*nitrobenzoate*, m. p. 99°). The allylnaphthol, which is obtained in 50—60% yield at 230°, condenses with henzenediazonium chloride to form 4-*benzeneazo*-2-*allyl*-a-*naphthol*, m. p. 157—158°, red crystals with green reflex.

The behaviour of ethyl o-allyloxyhenzoate has been recorded (*loc. cit.*). The position of the allyl group in the transformed product is proved by elimination of the carbethoxy group, whereby o-allylphenol is obtained. *Methyl* o-*allyloxybenzoate*, b. p. 143°/12 mm., D^{15} 1·118, changes by heating to *methyl* 3-*allylsalicylate*, h. p. 130°/10 mm., D 1·120, with almost explosive violence; the latter gives a bluish-violet coloration with alcoholic ferric chloride, and yields 3-*allylsalicylamide*, $C_3H_5 \cdot C_6H_3(OH) \cdot CO \cdot NH_2$, m. p. 99°, colourless plates, by prolonged keeping with concentrated methyl-alcoholic ammonia. By heating 2-allyloxybenzoic acid, the allyl does not displace the carboxyl group as in the cases recorded below, hut enters position 3, as is proved by the conversion of the resulting 3-allylsalicylic acid into o-allylphenol at 300°. *o*-Allylphenol condenses with henzenediazonium chloride to form the benzeneazo-*o*-allylphenol mentioned above. 2-*Methoxy*-3-*allylbenzoic acid*, m. p. 53°, is obtained by hydrolysing

the methyl ester, and 2-*acetoxy-3-allylbenzoic acid*,

$$C_3H_5\cdot C_6H_3(OAc)\cdot CO_2H,$$

m. p. 96°, colourless needles, by boiling 3-allylsalicylic acid with acetic anhydride and potassium acetate.

Methyl 2-allyloxy-3-allylbenzoate, b. p. 152—162°/9 mm., obtained by heating methyl 3-allylsalicylate with allyl bromide and methyl alcoholic sodium methoxide, yields 2-*allyloxy-3-allylbenzoic acid*, m. p. 57°, by hydrolysis. By heating at about 250—260°, the acid is converted into 3 : 5-*diallylsalicylic acid*, m. p. 99°, and 2 : 6-*diallylphenol*, b. p. 256—258°, whilst the methyl ester yields *methyl* 3 : 5-*diallylsalicylate*, b. p. 155—165°/9 mm., which develops a dark blue coloration with ferric chloride. 3 : 5-*Diallylsalicylic acid*, m. p. 99°, colourless needles, gives an indigo blue colour with ferric chloride, and forms an *acetyl* derivative, m. p. 94°.

The allylation of methyl 3 : 5-diallylsalicylate yields *methyl* 2-*allyloxy*-3 : 5-*diallylbenzoate*, b. p. 180—182°/10 mm. This ester decomposes completely by heating under ordinary pressure, but the corresponding *acid*, m. p. 55°, is converted into 2 : 4 : 6-*triallylphenol*, b. p. 293—295° or 152—153°/10 mm., D^{15} 0·978 (*phenylcarbamate*, m. p. 97°).

Methyl 2-allyloxy-3-methylbenzoate, b. p. 130—140°/10 mm., is converted by heating into *methyl 2-hydroxy-3-methyl-5-allylbenzoate*, b. p. 275—290°, whilst 2-*allyloxy-3-methylbenzoic acid*, m. p. 59°, yields chiefly 2-*methyl-3-allylphenol*, b. p. 231—233°, 2-*hydroxy-3-methyl-5-allylbenzoic acid*, m. p. 127—129°, being obtained as a by-product.

Ethyl p-*allyloxybenzoate*, b. p. 156°/10 mm., is changed at 220—250° to *ethyl 4-hydroxy-3-allylbenzoate*, m. p. 78°, b. p. 185°/9 mm., the hydrolysis of which yields 4-*hydroxy-3-allylbenzoic acid*, m. p. 125°.

4-*Allyloxybenzoic acid*, m. p. 162°, crystallises in colourless plates and leaflets. By heating with concentrated aqueous potassium hydroxide at 180°, 4-hydroxy-3-allylbenzoic acid is converted into 4-*hydroxy-3-propenylbenzoic acid*, m. p. 169°.

Ethyl 4-allyloxy-3-allylbenzoate, b. p. 176°/9 mm., obtained by the allylation of ethyl 4-hydroxy-3-allylbenzoate (corresponding acid, $C_{13}H_{14}O_3$, m. p. 140°), is easily converted into *ethyl 4-hydroxy-3 : 5-diallylbenzoate*, m. p. 94°, b. p. 184—194°/9 mm., at 220—230°. 4-*Hydroxy-3 : 5-diallylbenzoic acid* has m. p. 108°. By allylation its ester is converted into *ethyl 4-allyloxy-3 : 5-diallylbenzoate*, b. p. 190°/10 mm., which decomposes when heated under ordinary pressure: the *acid*, $C_{16}H_{18}O_3$, m. p 97°, however, is converted into 2 : 4 : 6-triallylphenol quantitatively at 300°.

2-*Allyloxybenzaldehyde*, b. p. 130°/10 mm., D^{15} 1·094, obtained almost quantitatively by boiling salicylaldehyde with allyl bromide and potassium carbonate in absolute alcohol, changes at 220—230° to 3-*allylsalicylaldehyde*, b. p. 245·5—246° or 111°/11 mm., D^{15} 1·098, which develops a bluish-violet coloration with alcoholic ferric chloride, forms a *copper* salt, $Cu(C_{10}H_9O_2)_2$, m. p. 181°, olive-brown needles, and *ferric* salt, $Fe(C_{10}H_9O_2)_3$, m. p. 110—111°, black crystals, condenses with benzenediazonium chloride in alkaline solution to form *benzeneazo-3-allylsalicylaldehyde*, $C_6H_5N_2\cdot C_6H_2(OH)(C_3H_5)\cdot CHO$, m. p. 71°, yellow needles or prisms, and forms an *aldoxime*,

$$C_3H_5\cdot C_6H_3(OH)\cdot CH{:}NOH,$$

m. p. 79°. The oxime is converted by acetyl chloride into the *acetyl*

...rivative, $C_3H_5\cdot C_6H_3(OH)\cdot CH:NOAc$, m. p. 58° (from which the ...yde is obtained by heating), and the *hydrochloride*,

$$C_3H_5\cdot C_6H_3(OH)\cdot CH:NOH,HCl.$$

...y methylation by the potassium carbonate method, 3-allylsalicyl-...dehyde is converted into *2-methoxy-3-allylbenzaldehyde*, b. p. 128°/...mm., which is oxidised to 2-methoxy-3-allylbenzoic acid by alkaline ...ydrogen peroxide. The formation of this acid is the proof that the ...lyl group is in position 3 in the allylsalicylaldehyde obtained by the ...an-formation of 2-allyloxybenzaldehyde.

2-Allyloxy-3-allylbenzaldehyde, b. p. 145—147°/11 mm., obtained by ...e allylation of 3-allylsalicylaldehyde, is converted at 200° into a ...:6-diallylphenol (75%) and 3 : 5-*diallylsalicylaldehyde*, b. p. 138—143°/...mm. (*semicarbazone*, m. p. 154—156°). 2 : 6-Diallylphenol condenses ...ith benzenediazonium chloride to form 4-*benzeneazo*-2 : 6-*diallylphenol*, ...p. 37°, reddish-yellow prisms.

2-Allyloxybenzyl alcohol, $C_3H_5O\cdot C_6H_4\cdot CH_2\cdot OH$, b. p. 133—150°/...mm., obtained by the allylation of saligenin, yields formaldehyde ...d resinous products by heating.

4-Allyloxybenzaldehyde, b. p. 142°/10 mm., changes violently at ...0—270°, and yields about 66% of *4-hydroxy-3-allylbenzaldehyde*, m. p. ...°, b. p. 179°/9 mm. By allylation, the latter yields *4-allyloxy-3-...llylbenzaldehyde*, b. p. 164°/10 mm., which changes at 250° to *4-hydroxy-...:5-diallylbenzaldehyde*, m. p. 67·5°, b. p. 185—190°/10 mm., to the ...xtent of about 66%. This in its turn, by allylation, yields *4-allyloxy-...:5-diallylbenzaldehyde*, which even by distillation under low pressures ...ses carbon monoxide and is converted into 2 : 4 : 6-triallylphenol.

The behaviour of *2-allyloxy-3-methoxybenzaldehyde* (o-*vanillin allyl ...her*), b. p. 156—160°/12 mm., obtained by the allylation of ...vanillin, is particularly interesting. By heating at 170—240°, it ...ields mainly *o*-eugenol, carbon monoxide being eliminated ; in addition, ...owever, *2-hydroxy-3-methoxy-5-allylbenzaldehyde* (5-*allyl*-o-*vanillin*), ...m. p. 48—49°, pale yellow crystals, and *4-hydroxy-3-methoxy-5-allyl-...enzaldehyde* (5-*allylvanillin*), m. p. 86°, b. p. 173°/9 mm., are formed. ...Allyl-*o*-vanillin is almost odourless, develops a dark blue coloration ...ith alcoholic ferric chloride, dissolves in 10% aqueous sodium carbonate, ...orms a *semicarbazone*, m. p. 195°, and in alcohol reacts with con-...centrated aqueous ammonia to form an *imino*-derivative,

$$C_3H_5\cdot C_6H_2(OMe)(OH)\cdot CH:NH,$$

...m. p. 114°, yellow needles. By allylation, it is converted into ...*methoxy-2-allyloxy-5-allylbenzaldehyde*, which changes at 170—285° ...nto *o*-allyleugenol.

3-Methoxy-4-allyloxybenzaldehyde (p-*vanillin allyl ether*) changes ...ery vigorously at ordinary pressure, and appreciably even at low ...ressures, to 5-allylvanillin ; at 210—220°, the yield is 80%. ...*Methoxy-4-allyloxy-5-allylbenzaldehyde*, obtained by its further ...llylation, changes to *o*-allyleugenol by distillation, the amount of ...arbon monoxide evolved corresponding with an 82% yield. C. S.

Preparation of the Thymyl Ester of *iso*Valeryloxyacetic Acid. J. D. RIEDEL (D.R.-P. 260471. Compare this vol., i, 63).—...*Thymyl chloroacetate*, a yellow oil, b. p. 262°, with a faint odour of ...thymol, is prepared by the condensation of thymol and chloroacetyl

chloride; when treated with sodium *iso*valerate it furnishes *thymyl iso-valeryloxyacetate*, $C_6H_3MePr^{\beta}\cdot O\cdot CO\cdot CH_2\cdot O\cdot CO\cdot CH_2\cdot CHMe_2$, a yellow liquid, b. p. 207—209°/19 mm., D 1·037, and of therapeutic value.

F. M. G. M.

Action of Bromine and of Chlorine on Phenols. Substitution Products, ψ-Bromides, and ψ-Chlorides. XXVI. Action of Bromine on Di-*o*-cresoldimethylmethane [6 : 6′-Dihydroxy-ββ-di-*m*-tolylpropane]. THEODOR ZINCKE, J. KEMPF, and W. UNVERZAGT (*Annalen*, 1913, **400**, 27—47).—*m*- and *p*-Cresols condense with acetone in the presence of hydrogen chloride to form indifferent substances, $C_{20}H_{24}O_2$, which are probably ethers (Zincke and Gaebel, A., 1912, i, 442). *o*-Cresol (7 parts), acetone (1 part), and 0·7 part of hydrochloric acid, D 1·19, react at the ordinary temperature to form 6 : 6′-dihydroxy-ββ-di-*m*-tolylpropane,

$$CMe_2(C_6H_3Me\cdot OH)_2,$$

m. p. 136°, colourless needles, which is quite analogous to *pp*-dihydroxy-ββ-diphenylpropane (Zincke and Grüters, A., 1906, i, 172; Zincke, *ibid.*, i, 737) in its behaviour. It forms a *diacetyl* derivative, $C_{21}H_{24}O_4$, m. p. 88—89°, and reacts with bromine in cold glacial acetic acid to form 5 : 5′-*dibromo*-6 : 6′-*dihydroxy-ββ-di*-m-*tolylpropane*,

$$CMe_2(C_6H_2MeBr\cdot OH)_2,$$

m. p. 119—120°, colourless plates or double pyramids (*diacetyl* derivative, m. p. 145°). When treated in the cold with an excess of bromine without a solvent, dihydroxy-ββ-di-*m*-tolylpropane or the preceding dibromo-derivative yields 3 : 4 : 5-tribromo-*o*-cresol, tetrabromo-*o*-cresol (in one experiment a *substance*, $C_{10}H_9Br_5$, m. p. 250—251°), and ψ-3-*bromo-5-pentabromo*iso*propyl*-o-*cresol* (ψ-*hexabromo*-5-iso*propyl*-o-*cresol*), $OH\cdot C{<}{\substack{CBr{-}CH\\CMe{:}CH}}{>}C\cdot CBr(CHBr_2)_2$, m. p. 169—170° (decomp.), colourless, monoclinic prisms, which is insoluble in aqueous sodium hydroxide. The hexabromo-ψ-bromide resembles ψ-heptabromo-*p*-*iso*propylphenol (Zincke and Grüters, *loc. cit.*) in its behaviour, and since the latter has the constitution $OH\cdot C_6H_2Br_2\cdot CBr(CHBr_2)_2$ (Zincke, A., 1912, i, 443), ψ-hexabromo-5-*iso*propyl-*o*-cresol probably has the constitution recorded above; it certainly contains only one bromine atom in the benzene nucleus. It readily yields an *acetyl* derivative, $C_{12}H_{10}O_2Br_6$, m. p. 135—136°, stout plates, by treatment with acetic anhydride and concentrated sulphuric acid. By the action of alcohol and 2*N*-sodium hydroxide at the ordinary temperature, the acetyl derivative is converted into 3-*bromo-5-tetrabromo*iso*propenyl*-o-*cresol*, $OH\cdot C{<}{\substack{CBr{-}CH\\CMe{:}CH}}{>}C\cdot C(CHBr_2){:}CBr_2$, m. p. 94—95°, which forms an *acetyl* derivative, $C_{12}H_9O_2Br_5$, m. p. 114—115°, and *methyl ether*, $C_{11}H_9OBr_5$, m. p. 110—111°. By oxidation with boiling dilute nitric acid and silver nitrate, the methyl ether is converted into 3-*bromo-2-methoxy*-m-*toluic acid*, $C_9H_9O_3Br$, m. p. 206—207°, the formation of which proves the presence of only one bromine atom in the benzene nucleus of the methyl ether and, therefore, also in that of the hexabromo-ψ-bromide.

ψ-3-Bromo-5-pentabromo*iso*propyl-*o*-cresol, dissolved in acetone, is

converted by careful treatment with water at the ordinary temperature into 3-*bromo*-5-*tetrabromo*iso*propylidenetoluquinone*,

$$CO\lt\begin{matrix}CBr:CH\\CMe:CH\end{matrix}\gt C:C(CHBr_2)_2,$$

m. p. 180—181°, golden-yellow prisms, which is quite stable. It is reconverted into the hexabromo-ψ-bromide by hydrogen bromide in glacial acetic acid, yields a *diacetate*,

$$OAc\cdot C\lt\begin{matrix}CBr-CH\\CMe:CH\end{matrix}\gt C\cdot C(CHBr_2)_2\cdot OAc,$$

m. p. 160—161°, colourless needlos, by treatment with acetic anhydride and concentrated sulphuric acid, and is converted into 3-*bromo*-5-*tetrabromomethoxy*iso*propyl*-o-*cresol*,

$$OH\cdot C\lt\begin{matrix}CBr-CH\\CMe:CH\end{matrix}\gt C\cdot C(CHBr_2)_2\cdot OMe,$$

m. p. 100—101°, colourless prisms (*acetyl* derivative, $C_{13}H_{13}O_3Br_5$, m. p. 163°), by boiling methyl alcohol and a few drops of concentrated sulphuric acid.

The *phenol-alcohol*, $OH\cdot C\lt\begin{matrix}CBr-CH\\CMe:CH\end{matrix}\gt C\cdot C(CHBr_2)_2\cdot OH$, m. p. 126°, colourless needles or prisms, corresponding with the preceding diacetate, cannot be prepared from the hexabromo-ψ-bromide or from the toluquinone by the addition of water, but is obtained from the latter in a curious manner by the action of glacial acetic acid and fuming sulphuric acid (20% SO_3) on the water-bath, water being subsequently added to the solution.

3-Bromo-5-tribromo*iso*propenyl-o-cresol is produced by the reduction of 3-bromo-5-tetrabromo*iso*propylidenetoluquinone by stannous chloride solution and hot glacial acetic acid, but has only been identified in the form of its *acetate*,

$$OAc\cdot C\lt\begin{matrix}CBr-CH\\CMe:CH\end{matrix}\gt C\cdot C(CHBr_2):CHBr,$$

m. p. 90—91°, rhombic prisms or plates.

By shaking with aniline and glacial acetic acid, the hexabromo-ψ-bromide or the toluquinone is converted into *pentabromo*iso*propyl*-o-*cresol*-ψ-*anilide*, $C_{16}H_{14}ONBr_5$, m. p. 128—129°, which is given the quinonoid constitution, $CO\lt\begin{matrix}CBr:CH\\CMe:CH\end{matrix}\gt CH\cdot C(CHBr_2)_2\cdot NHPh$, on account of its insolubility in alkalis. It forms colourless crystals which easily become yellow, and dissolves in boiling methyl or ethyl alcohol or glacial acetic acid; the yellow solutions deposit a *substance*, m. p. 223—224° (decomp.), intensely yellow prisms, which forms an orange-yellow *sodium* salt. The naturo of the yellow substance has not yet been ascertained. C. S.

[Preparation of Compounds containing Selenium.] August von Wassermann and Ernst Wassermann (D.R.-P. 261793).—When a solution of *p*-nitrosodimethylaniline in concentrated hydrochloric acid solution is treated with hydrogen selenide a bluish-red scum is formed; when this *leuco*-derivative (which was not isolated) is oxidised and subsequently treated with an aqueous solution of zinc chloride, a double

compound with zinc chloride is precipitated; this "selenoazine blue" is an analogue of methylene-blue, and can be employed as a dye and for the introduction of selenium into animal tissues; it forms a glistening, dark green bronze powder, readily soluble in water, sparingly so in alcohol. F. M. G. M.

Action of Methyl Iodide on Aromatic Tellurides. KARL LEDERER (*Annalen*, 1913, **399**, 260—271).—Aromatic tellurides, unlike aromatic sulphides and selenides, readily react additively with methyl iodide, forming diarylmethyltelluronium iodides. From these, other salts can be prepared, specially characteristic being the sparingly soluble picrates, chromates, dichromates, and platinichlorides; the chlorides form double salts with the chlorides of mercury, gold, zinc, and copper.

The diarylmethyltelluronium hydroxides, prepared from the iodides by means of moist silver oxide, are extremely hygroscopic, oily liquids which have a strong alkaline reaction, liberate ammonia from its salts, precipitate the heavy metals in the form of their hydroxides, but do not combine with carbon dioxide. Aryl tellurides react with ethyl iodide only to a very small extent.

Phenyl telluride and methyl iodide, after being kept for two days, yield a crystalline *compound*, $TePh_2MeI,MeI$, which is converted by ether into *diphenylmethyltelluronium iodide*, $TePh_2MeI$, m. p. or decomp. 123—124° (bath at 110°), colourless needles (from hot water), which is decomposed by alcohol, as also are the *bromide*, m. p. 137—138°, small prisms, and *chloride*, m. p. 129—130° (decomp.). The *nitrate*, m. p. 168—169°, rhombic plates; *platinichloride*, m. p. 157—158°, microscopic, yellow plates; *chromate*, m. p. 151°, orange-red needles; *dichromate*, decomp. 153°, orange-red, quadratic leaflets; *picrate*, $C_{19}H_{15}O_7N_3Te.H_2O$, m. p. 93—94°, long, yellow needles; *mercurichloride*, $C_{13}H_{13}TeCl,HgCl_2$, m. p. 135—136°, colourless needles, and *zincichloride*, m. p. 149—150°, are described. *Diphenylmethyltelluronium hydroxide* has an odour of piperidine or pyrrolidine, and is decomposed by warm water.

p-Tolyl telluride and methyl iodide, after being kept for five days, yield, after treating the product with ether, *di*-p-*tolylmethyltelluronium iodide*, m. p. 85—86° (decomp.); the *picrate*, m. p. 157—158°, yellow needles; *mercurichloride*, m. p. 149—150° (decomp.); *chloride*, *bromide*, m. p. 73—74°; *dichromate*, m. p. 54—55°; *chromate*, m. p. 51—52°; *platinichloride*, m. p. 104—105°, and *aurichloride*, m. p. 35—36°, have been prepared, but the salts and also the *hydroxide* are not particularly stable, several of the preceding salts certainly being impure.

Di-o-tolylmethyltelluronium iodide, m. p. 125—126°, small crystals, is obtained directly from its components after keeping for fourteen days. The *bromide*, m. p. 134—135° (bath at 120°), small prisms; *nitrate*, m. p. 155—157°, hexagonal plates; *picrate*, m. p. 143—144°; *platinichloride*, m. p. 186°, microscopic, yellow prisms; *dichromate*, m. p. 171—172° (decomp.), orange-red needles; *chromate*, m. p. 161—162°, small, yellow prisms; *mercurichloride*, m. p. 134—135° (decomp.), felted needles, and basic *zincichloride*, $TeMe(C_7H_7)_2Cl,ZnCl\cdot OH$, micro-

scopic prisms, have been prepared; the *hydroxide* is not hygroscopic, and is comparatively stable, not being decomposed by boiling water.

C. S.

Oxonium Compounds. GEORGE L. STADNIKOFF (*Ber.*, 1913, **46**, 2496—2503. Compare A., 1912, i, 109, 971).—In connexion with the conclusion drawn by the author from the occurrence of tetraphenylethane and αα-diphenylbutane after the action of water on the reaction product of diphenylmethyl butyl ether and magnesium propyl iodide, that the additive compound of the latter two substances is of the structure $\begin{matrix}C_4H_9\\CHPh_2\end{matrix}\!>\!O\!<\!\begin{matrix}Pr\\MgI\end{matrix}$, it may be objected that the formation of the tetraphenylethane and αα-diphenylbutane possibly preceded the addition of water.

To meet this objection, diphenylmethyl butyl ether has been allowed to react with various magnesium alkyl haloids in solution in ether (which does not prevent the formation of such additive compounds) for considerable periods. The procedure was to add the diphenylmethyl butyl ether to the cooled ethereal solution of the magnesium alkyl haloid and to find the quantities of any gaseous products evolved on boiling, and of the total organic products obtained on subsequently treating the cooled reaction product with water.

There are three main directions of decomposition of the ether additive compound which is believed to be the primary product on the addition of water: (1) the regeneration of diphenylmethyl butyl ether; (2) the formation of tetraphenylethane, and (3) the production of a αα-diphenyl-substituted paraffin hydrocarbon.

With diphenylmethyl butyl ether and magnesium propyl iodide all the above reactions occur, although the relative amounts of the different products vary from those obtained earlier (A., 1912, i, 971) with the same Grignard reagent in the absence of ethyl ether. The results, however, confirm the author's views.

Diphenylmethyl butyl ether was allowed to form additive compounds also with magnesium ethyl iodide and magnesium methyl iodide; the former gave similar results to the propyl compound; the latter gave as hydrocarbon products only methane and tetraphenylethane.

Magnesium propyl iodide either in benzene or in ethereal solution when treated with diphenylmethyl *iso*amyl ether, and subsequently with water, gave propane and unaltered diphenylmethyl *iso*amyl ether.

In each case, except with the methyl Grignard reagent, a quantity of the corresponding ethylenic hydrocarbon was evolved during the heating after the addition of the "mixed" ether.

D. F. T.

The Isomerism of Tri-α-naphthylcarbinol. ALEXEI E. TSCHITSCHIBABIN (*Ber.*, 1913, **46**, 2554—2556).—The author is of opinion that of the so-called isomeric forms of tri-α-naphthylcarbinol described by Schmidlin and Bergmann (this vol., i, 46), the more stable is in reality merely the ether-free carbinol described earlier by himself (A., 1911, i, 969), and is not identical with the stable "isomeride" obtained by Schmidlin and Massini (A., 1909, i, 563), which he has

shown to be an oxidation product, namely, α-naphthyldi-αα-naphthafluoryl alcohol. This view receives further confirmation from the fact that the free tri-α-naphthylcarbinol when dissolved in amyl acetate and treated with much ether is slowly deposited in needles or prisms of the easily oxidisable substance containing ether of crystallisation. The ether-free carbinol has a higher m. p., namely, 160—180° (decomp.), than that recorded hitherto.

There is consequently here no case of isomerism unless the compound containing ether of crystallisation is regarded as a distinct isomeride of the ether-free substance. D. F. T.

Aromatic Selenium Compounds. II. RUDOLF LESSER and R. WEISS (*Ber.*, 1913, **46**, 2640—2658. Compare A., 1912, i, 642). —An extended account of the results of attempts to prepare compounds containing a selenium atom in place of a sulphur atom, a preliminary note of which has previously appeared (*loc. cit.*).

Diphenyldiselinide-di-*o*-carboxylic acid, $Se_2(C_6H_4\cdot CO_2H)_2$, is more conveniently prepared by the addition of a diazotised solution of anthranilic acid to a solution of potassium or sodium diselinide in an atmosphere of carbon dioxide. After decomposition of the diazo-compound by heat, the acids are liberated by addition of mineral acid to the hot solution. The crude diphenyldiselinide-di-*o*-carboxylic acid is freed from diphenylselinide-di-*o*-carboxylic acid by digestion with glacial acetic acid, which leaves the former undissolved.

o-*Methylselenolbenzoic acid*, $SeMe\cdot C_6H_4\cdot CO_2H$, long needles, m. p. 180—181°, is obtained in practically quantitative yield when an alkaline solution of sodium *o*-selenolbenzoate is shaken with methyl sulphate. The corresponding *methyl* ester, m. p. 64—66°, is best obtained by the action of methyl iodide on the *silver* salt, and, in contrast with methyl *o*-methylthiolbenzoate, is odourless. o-*Benzoylselenolbenzoic acid*, $SeBz\cdot C_6H_4\cdot CO_2H$, has m. p. 163—164°.

o-Selenonbenzoic acid, $SeO_3H\cdot C_6H_4\cdot CO_2H$, is a very strong acid, the salts of which are not decomposed by dilute nitric acid. It has not been obtained in the crystalline state, but yields a *barium* salt, $C_7H_4O_5SeBa$, which separates from water in colourless, anhydrous needles. An aqueous solution of the acid is transformed by hydrochloric acid into o-*seleninbenzoic acid*, m. p. 228—229° (decomp.), which is also obtained by the oxidation of diphenyldiselenide-di-*o*-carboxylic acid by nitric acid, or a mixture of nitric and sulphuric acids. When heated at 130—140° until constant in weight, it is transformed into the *anhydride*, $O(SeO\cdot C_6H_4\cdot CO_2H)_2$, without change in m. p.

When diphenyldiselenide-di-*o*-carboxylic acid is warmed with thionyl chloride and excess of the latter removed, a crystalline residue is obtained which can be separated by means of light petroleum into two portions. The smaller of these, m. p. 173—174°, is the normal chloride, $C_{14}H_8O_2Cl_2Se_2$, whilst the larger, m. p. 65—66°, consists of a *compound* of this substance and hydrogen chloride, and has the composition $C_{14}H_{10}O_2Cl_4Se_2$. When the latter is boiled with methyl alcohol, the *hydrochloride* of *methyldiphenyl diselenide-di-o-dicarboxylate*, $C_{16}H_{16}O_4Cl_2Se_2$, yellow needles, m. p. 74—75°, is obtained, which, when treated with warm sodium hydroxide, is converted into the corresponding *ester*, m. p. 143—144°. The *hydrochloride* of the *ethyl*

ester, m. p. 91—92°, is similarly formed and converted in the same manner into the *ethyl* ester, m. p. 129—130°. The normal esters can also be prepared by the action of the requisite alcohol on the normal chloride or on the free acid in the presence of hydrogen chloride.

Phosphorus pentachloride resembles thionyl chloride in its action on the free acid, yielding, however, a less pure product which contains a rather greater proportion of the normal chloride.

Pure diphenylselenide-di-*o*-carboxylic acid has m. p. 234—235° (instead of 228—229° as previously given). Thionyl chloride converts it into the corresponding normal *chloride*, lemon-yellow crystals, m. p. 107—108°, which gradually decomposes when preserved without, however, yielding a uniform product. Boiling methyl and ethyl alcohols transform the chloride into the *methyl* ester, m. p. 70—71°, and the *ethyl* ester, m. p. 64—65°, respectively. The *amide* forms colourless plates, m. p. 212—213°.

When warmed with concentrated sulphuric acid on the water-bath, diphenylselenide-di-*o*-carboxylic acid yields two products which can be separated by means of sodium hydroxide. The soluble portion consists of *selenoxanthone-o-carboxylic acid*, $C_6H_4<\begin{smallmatrix}CO\\Se\end{smallmatrix}>C_6H_3\cdot CO_2H$, which sublimes from 250° in yellow needles and decomposes at 290—300°. In the dry state it is stable, but, when dissolved, readily eliminates carbon dioxide, for example, when a hot solution of its alkali salt is acidified. Attempts to transform it into the corresponding selenoxanthone by loss of carbon dioxide were, however, unsuccessful, benzophenone-selenone, $C_6H_4<\begin{smallmatrix}CO\\SeO_2\end{smallmatrix}>C_6H_4$, being invariably produced. This substance also constitutes the portion obtained in the above action which is insoluble in alkali and is obtained as by-product of the action of thionyl chloride on diphenylselenide-di-*o*-carboxylic acid. It forms large, glassy prisms, m. p. 317—318° (decomp.), and sublimes partly undecomposed from about 260°. It thus differs remarkably from the benzophenoneselenone described by Doughty and Elder (this vol., i, 962) for which the m. p. 183° is given.

Acetic anhydride is without action on diphenylselenide-di-*o*-carboxylic acid, whilst potassium permanganate, in neutral or alkaline solution, converts it into the selenone.

o-Carboxyphenylselenolacetic acid is readily converted into its *methyl* ester, leaflets, m. p. 62—63°, by means of methyl alcohol and hydrogen chloride. The ethyl ester is oily.

When a diazotised solution of *m*-aminobenzoic acid is added to a solution of potassium hydrogen selenide or of potassium diselenide under the conditions described for anthranilic acid, *diphenylselenide-di-m-carboxylic acid* is produced, the diselenide acid being apparently not formed. It has m. p. 296—297°, and sublimes from about 260°. Concentrated sulphuric acid dissolves it with a yellow colour; fuming sulphuric acid with an intense bluish-green colour. Potassium permanganate oxidises it in the form of its salts to *diphenylselenon-di-m-carboxylic acid*, colourless prisms, which becomes yellow at about 255°, and has m. p. 262—263° (decomp.).

p-Aminobenzoic acid, when similarly treated, yields a difficultly separable mixture of the *p*-diselenide and selenide acids. *Diphenyl-*

*diselenide-di-*p-*carboxylic acid* is a pale yellow, crystalline powder, m. p. 314—315°. *Diphenylselenide-di-*p-*carboxylic acid,* two preparations of which had m. p. 312—313° and 315—316°, resembles the above acid so closely that it can only be distinguished from it by ultimate analysis.

Hydroxyselenonaphthen reacts with 5-bromoisatin in alcoholic solution in the presence of piperidine to form "*2-selenonaphthen-[5-bromo-3-indole]-indigo*" (*3′-bromoindoxyl-2-selenonaphthen-3-one*),

$$C_6H_4{<}\substack{CO\\Se}{>}C{:}C{<}\substack{CO\longrightarrow\\C_6H_3Br}{>}NH,$$

red, silky needles, which sublime at about 260°, have m. p. about 355° and are soluble in fuming sulphuric acid, yielding a sulphonic acid which is soluble in water. Similarly, *3′-methylindoxyl-2-selenonaphthen-3-one* (red needles which sublime at about 250°, and have m. p. approximately 325—330°) is obtained from methylisatin, whilst by heating molecular quantities of isatin chloride and hydroxyselenonaphthen in benzene solution, "*2-selenonaphthen-2-indole-indigo*" [*2′-indoxyl-2-selenonaphthen-3-one*], $C_6H_4{<}\substack{CO\\NH}{>}C{:}C{<}\substack{CO\\Se}{>}C_6H_4$, is formed. It consists of blackish-violet needles, which sublime undecomposed at approximately 250°, and have m. p. about 335°.

A series of condensation products of hydroxyselenonaphthen with aldehydes and fluorenone has been prepared by boiling molecular quantities of their components in methyl- or ethyl-alcoholic or glacial acetic acid solution in the presence of a few drops of concentrated hydrochloric acid. In general, the compounds are rapidly precipitated in good yield. They dissolve unchanged in concentrated sulphuric acid, but are converted by the fuming acid into sulphonic acids which dissolve in water. The following compounds have been prepared: Glyoxal yields the *substance,*

$$C_6H_4{<}\substack{CO\\Se}{>}C{:}CH{\cdot}CH{:}C{<}\substack{CO\\Se}{>}C_6H_4,$$

violet needles, m. p. 299—300°. Heptaldehyde and citral give oily products. *Furylidene-2-selenonaphthen-3-one,*

$$C_6H_4{<}\substack{CO\\Se}{>}C{:}CH{\cdot}C_4H_3O,$$

orange needles, m. p. 145—147°, p-*nitrobenzylidene-2-selenonaphthen-3-one,* reddish-golden needles or rods, m. p. 243—244°; 2:4-*dinitrobenzylidene-2-selenonaphthen-3-one,* which exists in two modifications, red or orange needles, both having m. p. 226—227° (decomp.); o-*hydroxybenzylidene-2-selenonaphthen-3-one,* brownish-yellow rods, m. p. 206—207° (decomp.); o-*carboxybenzylidene-2-selenonaphthen-3-one,* $C_6H_4{<}\substack{CO\\Se}{>}C{:}CH{\cdot}C_6H_4{\cdot}CO_2H$, yellow plates, m. p. 226—227°; *4-hydroxynaphthylidene-2-selenonaphthen-3-one,* red needles, m. p. 244—248°; *2-methoxynaphthylidene-2-selenonaphthen-3-one,* yellow crystals, m. p. 127—128°; 2-hydroxynaphthaldehyde yields a *compound,* $C_{27}H_{16}O_2Se_2$, pale red crystals, m. p. 210—211° after previous darkening, which does not dissolve in sodium hydroxide, and appears to be derived from two molecules of hydroxyselenonaphthen and one of the aldehyde. Terephthalaldehyde yields the *substance,* $C_6H_4{<}\substack{CO\\Se}{>}C{:}CH{\cdot}C_6H_4{\cdot}CH{:}C{<}\substack{CO\\Se}{>}C_6H_4$, orange needles, which sub-

lime at about 296°, and have m. p. approximately 330°, whilst β-anthraquinonealdehyde gives the *compound*, $C_6H_4<^{CO}_{Se}>C:CH\cdot C_{14}H_7O_2$, orange-red needles, subliming at about 270°, and having m. p. 348—349°. Prolonged warming with fluorenone in alcohlic solution yields the *substance*, $C_6H_4<^{CO}_{Se}>C:C<^{C_6H_4}_{C_6H_4}$, deep red crystals, m. p. 169—171°.

p-*Nitrobenzeneazo-3-hydroxyselenonaphthen*,

$$C_6H_4<^{C(OH)}_{Se}>C\cdot N:N\cdot C_6H_4\cdot NO_2,$$

reddish-brown crystals, m. p. 239—241° (decomp.), is obtained by the addition of p-nitrobenzene diazonium chloride to a solution of the sodium salt of hydroxyselenonaphthen in the presence of sodium acetate. H. W.

Diphenyleneacetic Acid [Fluorene-9-carboxylic Acid]. WILHELM WISLICENUS and ALEXANDER RUTHING (*Ber.*, 1913, 46, 2770—2771).—An aqueous solution of fluorene-9-carboxylic acid and sodium hydroxide (1 mol.) remains clear when kept in an atmosphere of hydrogen. In the presence of oxygen, it rapidly becomes turbid and deposits fluorenone; the yield of the latter is about 20% of the theoretical, and is increased to about 50% when another mol. of sodium hydroxide is present. At higher temperatures the decomposition proceeds differently, an aqueous solution of sodium fluorene-9-carboxylate at the b. p. yielding fluoreno and sodium carbonate, most readily when sodium hydroxide has been added. C. S.

Syntheses by means of Ethyl Diphenyleneacetate [Fluorene 9 carboxylate]. WILHELM WISLICENUS and WILLY MOCKER (*Ber.*, 1913, 46, 2772—2793).—The *potassium* derivative of ethyl fluorene-9-carboxylate is best obtained by adding rather more than the theoretical quantity of alcohol to ethyl fluorene-9-carboxylate and potassium (1 atom) in dry ether, a current of hydrogen being passed through the apparatus. It is thus obtained as a yellow, microcrystalline powder containing EtOH, which decomposes rapidly in moist air, and is converted in dry air into the additive *compound*,

$$\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}>C(OK)\cdot CO_2Et,EtOH,$$

from which ethyl 9-hydroxyfluorene-9-carboxylate, m. p. 93°, is obtained by the action of sulphuric acid. The *sodium* derivative,

$$C_{16}H_{13}O_2Na,EtOH,$$

of ethyl fluorene-9-carboxylate is prepared in a similar manner and reacts in the same manner with atmospheric oxygen. In consequence of the easy oxidisability of the alkali derivatives of ethyl fluorene-9-carboxylate, syntheses with these reagents must be effected in an atmosphere of hydrogen, otherwise 9-hydroxyfluorene-9-carboxylic acid is the final product.

The following syntheses have been performed. By treatment with the calculated amount of iodine, a solution of the alkali derivative, prepared as above, readily yields ethyl bisdiphenylenesuccinate [9 : 9′-difluorene-9 : 9′-dicarboxylate] (Staudinger, A.,

1906, i, 824), which cannot be hydrolysed to the corresponding acid. The solution of the potassium derivative and methyl iodide gives a nearly quantitative yield of *ethyl* α-*diphenylene-propionate* [*9-methylfluorene-9-carboxylate*], $\begin{matrix}C_6H_4\\ | \\ C_6H_4\end{matrix}\!>\!CMe\cdot CO_2Et$, b. p. 188—190°/14 mm., m. p. 33°, which, however, is not obtained quite pure by this method. *9-Methylfluorene-9-carboxylic acid* yields 9-methylfluorene at 250°; the latter has b. p. 154—156°/15 mm. and m. p. 45°. α-*Diphenylenebutyric* [*9-ethylfluorene-9-carboxylic*] *acid*,

$$\begin{matrix}C_6H_4\\ | \\ C_6H_4\end{matrix}\!>\!CEt\cdot CO_2H,$$

obtained in a similar manner by means of ethyl iodide, forms an *ethyl* ester, b. p. 200—205°/14—15 mm., and decomposes at 230—240° into carbon dioxide and 9-ethylfluorene. The latter is a liquid, b. p. 169—171°/14 mm., not a solid as stated by Wislicenus and Densch, and does not react with potassium even at 250°. *9-Allylfluorene-9-carboxylic acid*, $\begin{matrix}C_6H_4\\ | \\ C_6H_4\end{matrix}\!>\!C(CO_2H)\cdot CH_2\cdot CH\colon CH$, colourless prisms containing $\frac{1}{2}C_6H_6$ (*ethyl* ester, b. p. 200—203°/14 mm.), yields *9-allylfluorene*, b. p. 174—176°/15 mm., at 240—250°. *9-Benzylfluorene-9-carboxylic acid*, $\begin{matrix}C_6H_4\\ | \\ C_6H_4\end{matrix}\!>\!C(CO_2H)\cdot CH_2Ph$, m. p. 201—202°, colourless leaflets (*ethyl* ester, m. p. 90—91°), yields 9-benzylfluorene at 240—250°; the latter is also produced by boiling the ester with alcoholic potassium hydroxide.

Ethyl αα-*bisdiphenyleneadipate* [*9 : 9′-ethylenedifluorene-9 : 9′-dicarboxylate*], $\begin{matrix}C_6H_4\\ | \\ C_6H_4\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2 & \!\!-\!\!-\!\!-\!\! & CH_2\\ CO_2Et & & CO_2Et\end{matrix}\!>\!C\!<\!\begin{matrix}C_6H_4\\ | \\ C_6H_4\end{matrix}$, m. p. 179—180°, colourless needles, prepared by the aid of ethylene dibromide, yields, by hydrolysis with alcoholic sodium hydroxide at the ordinary temperature and subsequent acidification, *9 : 9′-ethylenedifluorene-9 : 9′-dicarboxylic acid*, m. p. about 260° (decomp.), αδ-*bisdiphenylenebutane* [*9 : 9′-ethylenedifluorene*], $C_2H_4(C_{13}H_9)_2$, colourless needles, being produced when the hydrolysis is effected on the water-bath.

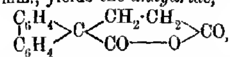
Iodobenzene does not react with the solution of the potassium derivative of ethyl fluorene-9-carboxylate even at 150—180°. 1-Bromo-2 : 4-dinitrobenzene, however, yields ethyl *9-op-dinitrophenylfluorene-carboxylate*, $C_{13}H_9(CO_2Et)\cdot C_6H_3(NO_2)_2$, m. p. 130—131°, faintly yellow crystals, which cannot be hydrolysed to the corresponding acid. In a similar manner, ethyl chloroacetate yields *ethyl diphenylene-succinate* [*9-carboxyfluorene-9-acetate*],

$$CO_2Et\cdot C_{13}H_8\cdot CH_2\cdot CO_2Et,$$

m. p. 73—75°, colourless crystals; by hydrolysis at the ordinary temperature, the ester yields the corresponding *acid*, $C_{16}H_{12}O_4$, m. p. 195—196° (decomp.), which is converted at its m. p. into its *anhydride*, $\begin{matrix}C_6H_4\\ | \\ C_6H_4\end{matrix}\!>\!C\!<\!\begin{matrix}CO-O\\ | \\ CH_2\cdot CO\end{matrix}$, m. p. 158—159°, b. p. about 255°/16 mm.

Ethyl β-iodopropionate reacts with the solution of the sodium or potassium derivative of ethyl fluorene-9-carboxylate to form, after hydrolysis of the impure ester, α-*diphenyleneglutaric* [*9-carboxyfluorene-*

-propionic] *acid*, $CO_2H\cdot C_{13}H_8\cdot CH_2\cdot CH_2\cdot CO_2H$, m. p. 195—196°, colourless prisms or needles. The acid forms an *ethyl* ester, $C_{21}H_{22}O_4$, b. p. 235—240°/14 mm., yields the *anhydride*,

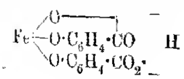


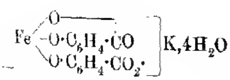
m. p. 175—176°, colourless prisms, by boiling with acetyl chloride, and is converted into *γ-diphenylenebutyric* [*fluorene-9-propionic*] *acid*, $C_{16}H_{14}O_2$, m. p. 148—149° (*ethyl* ester, b. p. 224—226°/17 mm.), by heating at about 260°.

Ethyl β-benzoyl-α-diphenylenepropionate [*9-phenacylfluorene-9-carboxylate*], $CO_2Et\cdot C_{13}H_9\cdot CH_2\cdot COPh$, m. p. 123—124°, obtained by means of ω-bromoacetophenone at about 80°, is converted by the action of aqueous alcoholic sodium hydroxide into *phenyl β-diphenylene-ethyl ketone* [*9-phenacylfluorene*], $C_{12}H_8\cdot CH\cdot CH_2\cdot COPh$, m. p. 96—97°, colourless needles. C. S.

Solubility of Salicylic Acid and of Some Other Substances. EDLIE SAVARRO (*Atti R. Accad. Sci. Torino*, 1913, **48**, 948—959).—Tables are given showing the solubility of salicylic acid at various temperatures, the figures obtained by previous observers being discordant. Some experiments have also been made on isomeric substances (compare Carnelley and Thompson, T., 1888, **53**, 782). The solubilities of the three hydroxybenzoic acids in water at 15° and at 50° increase in the order: ortho, para, meta, whilst those in methyl alcohol follow the order of the melting points: ortho, meta, para. According to the law of Carnelley and Thompson the order of solubilities should be para, meta, ortho. The solubilities in methyl alcohol of four pairs of isomeric pyridine derivatives prepared by Guareschi (*Atti R. Accad. Sci. Torino*, 1900–01, **50**) have also been determined; here the law already mentioned is followed with some exceptions. R. V. S.

Iron Compounds of Phenols. V. Iron Compounds of Salicylic Acid. RUDOLF F. WEINLAND and ALFRED HERZ (*Annalen*, 1913, **400**, 219—268. Compare this vol., i, 458).—The reaction between alkali salicylates and ferric salts in aqueous or alcoholic solution gives rise to very complex iron derivatives of salicylic acid. Their formation is due to the fact that salicylic acid forms, by virtue of its phenolic hydroxyl group, di- and tri-salicylatoferric acids analogous to the catecholferric acids (A., 1912, i, 445), and, by virtue of its carboxyl group, a hexasalicylatotriferric hydroxide analogous to hexabenzoatotriferric hydroxide (A., 1912, i, 854); this complex base can then react with the complex acids to form still more complex salts. In the preparation of the following substances, the concentrations of the reacting solutions and the order of their addition are matters of great importance. All quantities mentioned below are in atomic or molecular proportions.

(I.) 

(II.) 

Salts of Disalicylatoferric Acid (I).—*Potassium disalicylatoferrate* (II), dark copper-red powder, is obtained by adding aqueous ferric chloride to aqueous salicylic acid and potassium hydroxide (Fe : $C_7H_6O_3$: KOH = 1 : 4 : 7).

Rubidium disalicylatoferrrate, dark copper-red powder, is obtained in a similar manner ($Fe : C_7H_6O_3 : RbOH = 1 : 3 : 6$). These two salts form blood-red aqueous solutions, which change to violet by the addition of hydrochloric acid or of ferric chloride, and yield hexasalicylatotriferric monosalicylate (see below) by treatment with dilute acetic acid.

Salts of Trisalicylatoferric Acid, $\left[Fe\overset{O}{}_{(C_6H_4\cdot CO_2)_3}\right]H_3$.—The gradual addition of very dilute aqueous ferric chloride to concentrated aqueous sodium salicylate produces successively a reddish-yellow, blood-red, and finally violet solution. The blood-red solution contains sodium disalicylatoferrate, and the violet solution a ferric salt of this acid (see below). The reddish-yellow solution contains *sodium trisalicylatoferrate*, which, however, cannot be isolated from aqueous solution. *Potassium trisalicylatoferrate*, $[Fe(C_7H_4O_3)_3]K_3,1\frac{1}{2}H_2O$, brick-red, crystalline powder, is obtained from ferric acetate [of the composition $Fe_6(OAc)_{15}(OH)_3,3H_2O$], potassium salicylate, and potassium hydroxide in 96% alcohol ($Fe : C_7H_6O_3 : KOH = 1 : 4 : 7$). The *rubidium* salt, orange-red, crystalline powder containing $2H_2O$, is obtained in a similar manner. These salts are easily soluble in water, but the solutions rapidly decompose; however, if the alkali salicylate is also present, the solutions can be boiled without decomposition.

The free di- and tri-salicylatoferric acids have not been isolated. The union of the iron with the phenolic oxygen of the acid complex is proved by the fact that ferric acetate, methyl salicylate, and potassium hydroxide ($Fe : C_8H_8O_3 : KOH = 1 : 15 : 3$) in alcoholic solution yield *potassium tetramethylsalicylatoferrate*, $[Fe(C_7H_4O_3Me)_4]K$, reddish-brown, crystalline powder.

Salts of Hexasalicylatotriferric Hydroxide,

$$[Fe_3(O\cdot CO\cdot C_6H_4\cdot OH)_6](OH)_3.$$

—The reddish-yellow, blood-red, and violet solutions obtained, according to the quantities of the reagents used, by the addition of aqueous ferric chloride (at least 1 mol.) to a not too dilute aqueous solution of sodium salicylate (4 mols.) soon yield reddish-brown precipitates. By keeping in the mother liquor, these precipitates soon change to a black, crystalline substance (compare Hopfgartner, A., 1908, i, 891). The reddish-brown substance can be isolated unchanged if ether is added to either solution before the solutions of ferric chloride and sodium salicylate ($Fe : Na = 1 : 3$) are mixed; by shaking, the salicylic acid liberated in the reaction is removed from the aqueous phase, and the precipitate then remains unchanged. The same substance is also obtained unchanged when hot solutions of ferric chloride and sodium salicylate are mixed. It has been isolated as a brown powder containing $3H_2O$, and also as a reddish-brown, crystalline powder containing $2EtOH,2H_2O$. Since the ratio of iron to salicylic acid is 3 : 7 and the substance behaves like hexabenzoatotriferric monobenzoate (A., 1912, i, 854), it is regarded as *hexasalicylatotriferric monosalicylate*, $\left[Fe_3{}^{(O\cdot CO\cdot C_6H_4\cdot OH)_6}_{(OH)_2}\right]\cdot O\cdot CO\cdot C_6H_4\cdot OH$. A *sesquisalicylate*,

$$\left[Fe_3{}^{(O\cdot CO\cdot C_6H_4\cdot OH)_6}_{(OH)_2}\right]C_7H_5O_3,\left[Fe_3{}^{(C_7H_5O_3)_6}_{(OH)}\right](C_7H_5O_3)_2,7H_2O,$$

of the base is obtained as a red, crystalline powder (which rapidly becomes almost black) by treating the preceding substance with a

warm saturated solution of salicylic acid in acetone; chloroform or ethyl alcohol may also be used as the solvent, in the latter case the sesquisalicylate being obtained as a reddish-brown, crystalline powder containing 3EtOH and $9H_2O$.

The ferrisalicylic acid described by Hantzsch and Desch (A., 1902, i, 708) contains acetic acid and is in reality *hexasalicylatotriferric diacetate*, $\left[Fe_3{(O\cdot CO\cdot C_6H_4\cdot OH)_6 \atop (OH)}\right](OAc)_2,3Et_2O$, garnet-red prisms (from ether); by heating at 100°, it changes to the *monoacetate*, $\left[Fe_3{(O\cdot CO\cdot C_6H_4\cdot OH)_6 \atop (OH)_2}\right]\cdot OAc$. Other salts of hexasalicylatotriferric hydroxide have been obtained by the reaction between lithium salicylate and ferric chloride, bromide, or nitrate in alcoholic solution; in some of these reactions a little water must be added. None of these salts contains iron and salicylic acid in a ratio less than 3:6; therefore, they are regarded as complex derivatives of the hexasalicylatotriferric base. Thus lithium salicylate and ferric chloride yield, according to the proportions of the reagents, a *chloride salicylate*, $\left[Fe_3{(O\cdot CO\cdot C_6H_4\cdot OH)_6 \atop (OH)}\right]{O\cdot CO\cdot C_6H_4\cdot OH \atop Cl},4\frac{1}{2}H_2O$, red, crystalline powder, or a double *salt* of the chloride and the chloride salicylate,

$$\left[Fe_3{(C_7H_5O_3)_6 \atop (OH)_2}\right]Cl,\left[Fe_3{(C_7H_5O_3)_6 \atop (OH)}\right]{C_7H_5O_3 \atop Cl},H_2O,$$

red, amorphous powder (which becomes crystalline after two days), or a double *salt* of the salicylate and the chloride salicylate,

$$\left[Fe_3{(C_7H_5O_3)_6 \atop (OH)_2}\right]C_7H_5O_3,2\left[Fe_3{(C_7H_5O_3)_6 \atop (OH)}\right]{C_7H_5O_3 \atop Cl},11H_2O,$$

brownish-red, crystalline powder. Ferric bromide ($Fe_3Br_8,6H_2O$, see below) forms a double *salt*,

$$\left[Fe_3{(C_7H_5O_3)_6 \atop (OH)_2}\right]C_7H_5O_3,2\left[Fe_3{(C_7H_5O_3)_6 \atop (OH)}\right]{C_7H_5O_3 \atop Br},11H_2O,$$

carmine, crystalline powder, and ferric nitrate yields a double *salt*,

$$\left[Fe_3{(C_7H_5O_3)_6 \atop (OH)_2}\right]C_7H_5O_3,\left[Fe_3{(C_7H_5O_3)_6 \atop (OH)}\right]{C_7H_5O_3 \atop NO_3},2H_2O,$$

reddish-yellow, crystalline powder.

The great similarity between the salts of hexabenzoatotriferric hydroxide and hexasalicylatotriferric hydroxide indicates that in the latter the iron is attached to the carboxyl group of the salicylic acid, as represented in the preceding formulæ. This is also proved by the fact that salts of a similar base, *hexa-o-methoxybenzoatotriferric hydroxide*, can be obtained from *o*-methoxybenzoic acid. Thus by treating aqueous ferric chloride with aqueous sodium *o*-methoxybenzoate (Fe : Na = 1 : 3) or with warm aqueous *o*-methoxybenzoic acid (Fe : acid = 1 : 3), *hexa-o-methoxybenzoatotriferric mono-o-methoxybenzoate*,

$$\left[Fe_3{(O\cdot CO\cdot C_6H_4\cdot OMe)_6 \atop (OH)_2}\right]\cdot O\cdot CO\cdot C_6H_4\cdot OMe,7\tfrac{1}{2}H_2O,$$

is obtained as a yellow, crystalline substance; its alcoholic solution reacts with 20% perchloric acid to form the *perchlorate*,

$$\left[Fe_3{(O\cdot CO\cdot C_6H_4\cdot OMe)_6 \atop (OH)_2}\right]ClO_4,H_2O,$$

orange-yellow leaflets.

In a similar manner, by treating aqueous ferric chloride with sodium *m*- or *p*-hydroxybenzoate ($Fe : Na = 1 : 3$), *hexa*-m-*hydroxybenzoatotriferric mono*-m-*hydroxybenzoate*

$$\left[Fe_3{}^{(O \cdot CO \cdot C_6H_4 \cdot OH)_6}_{(OH)_2}\right] \cdot O \cdot CO \cdot C_6H_4 \cdot OH, 5H_2O,$$

dark brown powder, and the corresponding para-*isomeride*, brown, prismatic crystals, are obtained. The latter reacts with 5% aqueous ferric chloride in excess to form *p*-hydroxybenzoic acid and a very soluble *substance*, garnet-red prisms, which contains $Fe : Cl : C_7H_5O_3 = 1 : 1 : 1$, and is regarded as having the constitution

$$\left[Fe_3(O \cdot CO \cdot C_6H_4 \cdot OH)_6\right]\left[Fe^{Cl_2}_{(OH)_2}\right]_3, 10H_2O.$$

Hexa-p-*hydroxybenzoatotriferric chloride* p-*hydroxybenzoate*,

$$\left[Fe_3{}^{(O \cdot CO \cdot C_6H_4 \cdot OH)_6}_{(OH)}\right]^{Cl}_{O \cdot CO \cdot C_6H_4 \cdot OH}, 1\tfrac{1}{2}H_2O,$$

brown, crystalline powder, is obtained by the reaction of ferric chloride and lithium *p*-hydroxybenzoate ($Fe : Li = 1 : 1{\cdot}5$) in alcohol containing a little water.

Compounds of Hexasalicylatotriferric Hydroxide and the Salicylatoferric Acids or a Salicylatoferrous Acid.—The reddish-brown precipitate obtained from aqueous ferric chloride and sodium salicylate ($Fe : Na = 1 : 3$) changes by keeping in the mother liquor for about a day to a black, crystalline *substance* (the streak is violet), which contains $Fe : C_7H_5O_3 = 4 : 9$, not $1 : 2$ (compare Hopfgartner, *loc. cit.*), and is regarded as *hexasalicylatotriferric salicylate disalicylatoferrate* (annexed formula).

$$\left[Fe_3{}^{(O \cdot CO \cdot C_6H_4 \cdot OH)_6}_{(OH)}\right]\left[Fe\begin{cases}O \\ O \cdot C_6H_4 \cdot CO \\ O \cdot C_6H_4 \cdot CO_2\end{cases}\right]^{O \cdot CO \cdot C_6H_4 \cdot OH}, 8\tfrac{1}{2}H_2O.$$

In a similar manner, by keeping the initial reddish-brown precipitates in the mother liquors, ferric nitrate and sodium salicylate ($Fe : Na = 1 : 3$) yield a double *compound* of the preceding salt and hexasalicylatotriferric monosalicylate,

$$\left[Fe_3{}^{(C_7H_5O_3)_6}_{(OH)}\left[Fe\begin{cases}O \\ O \cdot C_6H_4 \cdot CO \\ O \cdot C_6H_4 \cdot CO_2\end{cases}\right]^{C_7H_5O_3}\right], \left[Fe_3{}^{(C_7H_5O_3)_6}_{(OH)_2}\right]C_7H_5O_3, 15H_2O,$$

black, crystalline powder, ferric sulphate and sodium salicylate ($Fe : Na = 1 : 1{\cdot}5$) yield a double *salt* of the bisdisalicylatoferrate and the salicylatedisalicylatoferrate of the hexa-base,

$$\left[Fe_3{}^{(C_7H_5O_3)_6}_{(OH)}\right][Fe(C_7H_4O_3)_2]_2, \left[Fe_3{}^{(C_7H_5O_3)_6}_{(OH)}\right]^{O \cdot CO \cdot C_6H_4 \cdot OH}_{[Fe(C_7H_4O_3)_2]}, 23H_2O,$$

violet-black, crystalline powder, and ferric acetate and sodium salicylate ($Fe : Na = 1 : 3$ and $1 : 4$ respectively) yield *substances*,

$$\left[Fe_3{}^{(C_7H_5O_3)_6}_{(OH)_2}\right][Fe(C_7H_4O_3)_2], 8\tfrac{1}{2}H_2O$$

and

$$\left[Fe_3{}^{(C_7H_5O_3)_6}_{(OH)_2}\right][Fe(C_7H_4O_3)_2], \left[Fe_3{}^{(C_7H_5O_3)_6}_{(OH)_2}\right] \cdot O \cdot CO \cdot C_6H_4 \cdot OH, 14H_2O,$$

violet, crystalline powders; the former of the last two substances is

also obtained from the reddish-brown precipitate resulting from the addition of dilute acetic acid to cold saturated aqueous potassium disalicylatoferrate (see above).

The compositions of the preceding complex salts are deduced from the ratio of the iron to the salicylic acid in them, and are most simply explained by assuming that the violet and black substances are salts of hexasalicylatotriferric hydroxide and salicylic or di- or tri-salicylatoferric acid. Thus the violet substance, two methods of preparing which are mentioned above, contains iron and salicylic acid in the ratio 4 : 8 (1 : 2), and is therefore hexasalicylatotriferric disalicylatoferrate. Again, the reddish-yellow, aqueous solution obtained from ferric chloride, salicylic acid, and potassium hydroxide

$$(Fe : C_7H_6O_3 : KOH = 1 : 3 : 5)$$

deposits a reddish-brown precipitate which changes to a *substance*, black, crystalline powder (violet streak), which contains

$$Fe : C_7H_6O_3 : K = 12 : 27 : 2\ ;$$

since reddish-yellow solutions are indicative of the alkali salt of trisalicylatoferric acid, the black substance is regarded as

$$\left[Fe_3{(C_7H_5O_3)_6 \atop (OH)}\right]K[Fe(C_7H_4O_3)_3],[Fe_3(C_7H_5O_3)_6][Fe(C_7H_4O_3)_3],25H_2O.$$

The preceding complex salts of the hexa-base differ from the simpler salts of the base mentioned under the third section in their black or violet colour, and in their insolubility in alcohol, acetone, and ether. Hexasalicylatotriferric monosalicylate changes to the violet and black salts of the hexa-base in the presence of water, and, conversely, the violet and black salts are converted into hexasalicylatotriferric monosalicylate by alcoholic salicylic acid; hence the changes hexa-base $\underset{\text{alcohol and } C_7H_6O_3}{\overset{H_2O}{\rightleftarrows}}$ disalicylatoferric acid are partly the cause of the large number of the iron compounds of salicylic acid.

The violet and black salts are very sparingly soluble in water, forming faintly violet solutions. Possibly the intensely violet coloration developed in the usual ferric chloride test for salicylic acid is due to the formation of a salt of disalicylatoferric acid containing a complex iron cation such as $[Fe(H_2O)_6]$ (salts of disalicylatoferric acid containing a simple cation such as potassium or sodium are red); such a salt would be more soluble than the violet or black salts described above, and would, therefore, produce a more intenssly violet coloration. The authors have been unable to isolate such a salt; they have prepared, however, a *salt* of the hexasalicylatotriferric and hexa-acetotriferric hydroxides with disalicylatoferric acid, $\left[Fe_3{(C_7H_5O_3)_6 \atop (OH)_2}\right][Fe(C_7H_4O_3)_2],[Fe_3(OAc)_6](OH)_3,4H_2O$, which is much more soluble in water than the violet and black salts, forming a reddish-violet solution changing to violet by the addition of hydrochloric acid, owing to the decomposition of the hexa-aceto-base.

Intensely violet solutions are obtained from aqueous sodium salicylate and an excess of ferric chloride, from aqueous salicylic acid and ferric chloride, and from all the salts of hexasalicylatotriferric hydroxide by warming them with very dilute hydrochloric acid; in all

these cases, disalicylatoferric acid and (complex) iron cations, that is, the two components necessary for the production of the intensely violet ferric disalicylatoferrate, are formed. Conversely, the addition of soium sal icylate or of sodium carbonate to solutions of salts of hexasalicylatotriferric hydroxide produces, according to the relative quantities of the reagents, red solutions of sodium disalicylatoferrate or reddish-yellow solutions of sodium trisalicylatoferrate. Similarly, the addition of aqueous calcium hydrogen carbonate to the violet solution produces a red solution of calcium disalicylatoferrate.

The residue obtained by the evaporation of aqueous ferric bromide has the composition $Fe_3Br_8,6H_2O$, and contains ferrous iron. In alcoholic solution it reacts with lithium salicylate (Fe : Li = 1 : 3) to form a *substance*, olive-brown crystals, which contains

$$Fe^{'''} : Fe^{''} : C_7H_6O_3 = 3 : 1 : 9,$$

and is therefore regarded as *hexasalicylatotriferric salicylate disalicylatoferrite*, $\left[Fe_3^{'''}(C_7H_5O_3)_6\right]\begin{matrix}O\cdot CO\cdot C_6H_4\cdot OH\\ [Fe^{''}(C_7H_4O_3)_2]\end{matrix},6H_2O$. The same substance is obtained from lithium salicylate and alcoholic ferric chloride which has been partly reduced by the addition of iron. An alcoholic solution of $Fe_3Br_8,6H_2O$, which has been still further reduced by iron, reacts with lithium salicylate (Fe : Li = 1 : 3) to form *hexasalicylatotriferric hydrogen trisdisalicylatoferrite*,

$$[Fe_3^{'''}(C_7H_5O_3)_6]H_2[Fe^{''}(C_7H_4O_3)_2]_3,5\tfrac{1}{2}H_2O,$$

blackish-brown, crystalline powder. C. S.

Methylcarbonato-derivatives of Hydroxy-acids. EMIL FISCHER and HERMANN O. L. FISCHER (*Ber.*, 1913, **46**, 2659—2664).—Hydroxy-acids either do not react with methyl chloroformate in aqueous alkaline solution or give very poor yields of methylcarbonato-derivatives. The latter, however, are readily obtained by the combined action of methyl chloroformate and tertiary bases on hydroxy-acids dissolved in anhydrous solvents (compare Fischer, A., 1909, i, 161).

r-*Methylcarbonatomandelic acid*, $CO_2Me\cdot O\cdot CHPh\cdot CO_2H$, is obtained by the addition of methyl chloroformate to a well cooled solution of had *r*-mandelic acid in a mixture of chloroform and dimethylaniline. It m. p. 118—119° (corr.), after slight softening, and begins to decompose at about 140°. Alkalis readily transform it into *r*-mandelic acid, for which the authors give m. p. 120·5° (corr.) after previous softening, instead of 118° as recorded in the text books. r-*Methylcarbonatomandelyl chloride*, colourless prisms, m. p. 39—40°, is obtained by the action of phosphorus pentachloride at the ordinary temperature on a solution of the acid in chloroform, and is converted by cold methyl alcohol into *methyl r-methylcarbonatomandelate*, $CO_2Me\cdot O\cdot CHPh\cdot CO_2Me$, prisms, m. p. 51—52°. This ester is rapidly saponified by sodium hydroxide when dissolved in aqueous acetone; when two and a-half molecules of alkali are used, mandelic acid is formed, but when only one molecule is employed, methylcarbonatomandelic acid is the main product.

When mixed with an excess of aniline in ethereal solution, methylcarbonatomandelyl chloride yields a *compound*, $C_{16}H_{15}O_4N$, needles,

m. p. about 142° (corr. decomp.), which is converted by prolonged contact with $2N$-sodium hydroxide (2 mols.) into an acid which melts with decomposition, and has not been completely investigated. In any case, normal formation of the anilide of mandelic acid does not occur, and the authors therefore do not assign a definite structure to the aniline compound.

Glycollic acid reacts with methyl chlorocarbonate in a manner similar to mandelic acid, but yielding a product which is difficult to purify.

The authors have also prepared a compound from *r*-mandelic acid and acetylcarbimide in the expectation that the latter group would be readily eliminated, and that the product could thus be used in place of the methylcarbonato-derivatives. This is, however, not the case, since the re-conversion into mandelic acid does not occur with sufficient ease.

r-*Acetylaminocarboylmandelic acid*, $NHAc\cdot CO\cdot O\cdot CHPh\cdot CO_2H$, colourless needles, m. p. about 168—169° (decomp.), is obtained by the gradual addition of acetylcarbimide to a solution of well dried *r*-mandelic acid in anhydrous ether. It is converted by $2N$-sodium hydroxide at the ordinary temperature into the *urethane* of *mandelic acid*, $NH_2\cdot CO\cdot O\cdot CHPh\cdot CO_2H$, m. p. 172—173° (corr. decomp.), when quickly heated.

H. W.

Hydrogenation of Santonin. HEINRICH WIENHAUS (*Ber.*, 1913, 46, 2836—2839).—Polemical. The author assumes the presence of two conjugated double bonds in santonin based on the fact that at the ordinary temperature and without increased pressure in neutral solution it takes up four atoms of hydrogen (compare Weinhaus and Oettingen, this vol., i, 474; Wedekind and Beniers, this vol., i, 476; Angeli, this vol., i, 864).

Chromosantonin gives the same products on hydrogenation in presence of colloidal palladium chloride as santonin.

E. F. A.

Hydrogenation of Santonic Acid. Dihydrosantonin. GUIDO CUSMANO (*Annalen*, 1913, 400, 332—337).—Results already recorded (this vol., i, 864).

C. S.

Action of Sodium Hypochlorite on Amides of Unsaturated Acids. RUDOLF A. WEERMAN (*Annalen*, 1913, 401, 1—20. Compare A., 1906, i, 665; 1907, i, 132; 1908, i, 22; 1909, i, 589).—Freundler, van Linge, Jeffreys, and Baucke have attempted unsuccessfully to apply Hofmann's reaction to the production of amines from unsaturated acid amides.

Finely-powdered cinnamamide, by shaking with amyl alcohol and aqueous sodium hypochlorite, is converted into the *chloroamide*, $CHPh:CH\cdot CO\cdot NHCl$, m. p. 125° (decomp.), white plates, which yields *barium styrylcarbamate*, $Ba(C_9H_8O_2N)_2$, by treatment with aqueous barium hydroxide. The salt yields only a trace of phenylacetaldehyde by treatment with even the weakest acids; however, by decomposition with sodium hydrogen sulphite or hydroxylamine hydrochloride, the aldehyde is obtained in the form of its sodium hydrogen sulphite compound or oxime respectively.

The following substances are obtained by reactions similar to the preceding.

o-Nitrocinnamchloroamide, m. p. 142° (decomp.), colourless needles, is converted into *barium* o-*nitrostyrylcarbamate* by 0·3*N*-barium hydroxide on the water-bath; the latter yields o-*nitrophenylacetaldoxime*, m. p. 110°, colourless needles, with aqueous hydroxylamine hydrochloride.

m-*Nitrocinnamide*, m. p. 195—196°, prepared from the acid chloride and gaseous ammonia in benzene, is converted into *methyl* m-*nitrostyrylcarbamate*, m. p. 140°, yellow needles, from which m-*nitrophenylacetaldehyde*, $C_8H_7O_3N,H_2O$, m. p. 78—79°, can be prepared. m-*Nitrocinnamchloroamide*, m. p. 178° (decomp.), is converted as above into *barium* m-*nitrostyrylcarbamate*, yellow leaflets, from which m-*nitrophenylacetaldoxime*, m. p. 105—106°, colourless leaflets, can be obtained.

p-Nitrocinnamamide, m. p. 217° (not 155—160°, as stated by Chiozza in 1853), is converted by methyl alcohol and aqueous sodium hypochlorite into *methyl* p-*nitrostyrylcarbamate*, m. p. 188°, yellow needles, from which *p*-nitrophenylacetaldehyde, m. p. 85°, can be prepared. p-*Nitrocinnamchloroamide*, m. p. 169° (decomp.), colourless needles, is converted into *barium* p-*nitrostyrylcarbamate*, yellow needles, from which p-*nitrophenylacetaldoxime*, m. p. 155°, can be prepared. C. S.

Camphenecarboxylamide and Hydrocamphenecarboxylamide. JOSEF HOUBEN and ERNST WILLFROTH (*Ber.*, 1913, 46, 2530—2537).—The authors have recently shown (this vol., i, 970) that the action of methyl-alcoholic potash on methyl chloro*allo*camphanecarboxylate yields two isomeric unsaturated acids, the occurrence of which may be attributed to the unsymmetrical nature of chloro*allo*camphanecarboxylic acid or to the disturbing effect of the alkali on the single course of the reaction. The latter view receives support from the fact that chloro*allo*camphanecarboxylamide passes into a crystalline unsaturated amide, m. p. 210°, when merely boiled with water (*loc. cit.*), and the product appears to be free from any isomeride. Reduction of the unsaturated amide in acetic acid by platinum black and hydrogen causes a quantitative conversion into a saturated amide, *hydrocamphenecarboxylamide*, leaflets, m. p. 189°, which is quite distinct from *allo*camphanecarboxylamide. If the difference is not due to stereoisomerism, the above elimination of hydrogen chloride must therefore be accompanied by a change from the bornylene to the camphene group.

The mixture of unsaturated esters from methyl chloro*allo*camphanecarboxylate was then converted into the corresponding mixture of acids and treated with thionyl chloride; the resulting acid chlorides, when submitted together in ethereal solution to the action of ammonia, yielded two isomeric unsaturated amides, m. p. 209° and 98° respectively. The former, which preponderated, was identical with the amide (above) obtained by the action of water on the chlorine-substituted amide, and must be related to the camphenecarboxylic acid of m. p. 105°, whilst the latter amide, m. p. 98°, must be related to the second camphenecarboxylic acid.

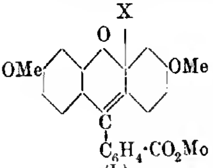
The action of sodium nitrite and hydrochloric acid on the saturated amide, m. p. 189° (see above), gave a saturated acid, *hydrocamphene-carboxylic acid*, hexagonal leaflets, m. p. 126°, which is also obtainable by hydrolysis with hot concentrated hydrochloric acid. D. F. T.

Preparation of Purpurin-3-carboxylic Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 260765. Compare Perkin and Cope, T., 1894, **65**, 848).—Purpurin-3-carboxylic acid, a red powder, m. p. 222—224° (with loss of carbon dioxide), is obtained when 1 : 2-dihydroxyanthraquinone-3-carboxylic acid dissolved in 20 parts of concentrated sulphuric acid is slowly treated at 15—20° with manganese dioxide (0·3—0·4 part); it is identical with the "ψ-purpurin" (purpurincarboxylic acid) present in madder. F. M. G. M.

Preparation of 1 : 4-Diaminoanthraquinone-2-carboxylic Acid and of 1 : 4-Diaminosulphoanthraquinone-2-carboxylic Acid. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 261885. Compare this vol., i, 1206).—1 : 4-*Diaminoanthraquinone-2-carboxylic acid*, dark blue, glistening, bronze needles, m. p. 350° (about), is obtained from 2-amino-5-acetylamino-4-carboxybenzoyl-*o*-benzoic acid (this vol., i, 621); the *sulphate* forms brownish-red needles; when heated with anhydrous boric acid (1 part) and 6 parts of fuming sulphuric acid (5% SO_3) at 190° and subsequently at 130—140° with the addition of 1 part of sulphuric acid (50% SO_3), it gives rise to 1 : 4-*diaminosulphoanthraquinone-2-carboxylic acid sulphate* as a brownish-red, crystalline precipitate. F. M. G. M

Oxonium and Alkali Salts of Fluorones. HANS VON LIEBIG (*Ber.*, 1913, **46**, 2736—2745).—The composition of the chloride of fluorescein trimethyl ether-ester [Kehrmann and Scheunert's (A., 1910, i, 407) methyl 3 : 6-dimethoxy-9-phenylxanthonium-2′-carboxylate] varies according to the treatment to which it is subjected. When prepared by the author's method (this vol., i, 865) and kept for five days at the ordinary temperature, a methyl-alcoholic solution of the chloride deposits fluorescein dimethyl ether of m. p. 198°; after removal of the latter compound, the addition of ether precipitates a *chloride*, $2C_{23}H_{20}O_6,3HCl,MeOH,2H_2O$, which has m. p. 110—125° (decomp.), and on crystallisation from water has the composition $C_{23}H_{20}O_6,HCl,MeOH,2H_2O$. The above chlorides resemble those previously described in yielding with 33% aqueous potassium hydroxide a blue *o*-quinonoid potassium salt. The hydrate, $C_{23}H_{20}O_6,H_2O$, obtained by acidifying an aqueous solution of the potassium salt with acetic acid, probably has the constitution represented in formula II. (*loc. cit.*, 867). On treatment with water the potassium salt yields a substance, $C_{23}H_{20}O_6$, which was previously considered to be a trimethyl ether-ester of fluorescein. The same substance is obtained by treating the potassium salt with methyl alcohol. It crystallises from cold methyl alcohol in slender, white needles, which sinter at 105—110° and gives off vapour at 126°, and again at a temperature a little above

180°; by warm methyl alcohol it is transformed into fluorescein dimethyl ether. It does not yield blue salts with alkalis, and therefore must contain the pyrone ring. It probably has the annexed constitution (I, where X = OMe).

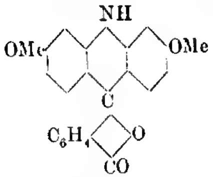


(I.)

Solutions of the preceding methoxy-compound and the hydrate mentioned above, in 10—15% hydrochloric acid, deposit a *chloride*, which melts with evolution of gas at 150°, then solidifies, and has m. p. 205°. This chloride differs from the chlorides of fluorescein trimethyl ether-ester already described in being practically insoluble in water. It yields blue salts with alkalis and probably has the formula I (X = Cl).

By heating the disodium salt of fluorescein with methyl sulphate and shaking the product with ether and ammonia, the author has obtained a substance, m. p. 255°, which he considered to be a dimethyl ether of fluorescein (A., 1912, i, 381). The same substance is formed by treating the chloride of fluorescein trimethyl ether ester with strong aqueous ammonia. When pure it has m. p. 256—257°, and is stable towards boiling alcoholic hydrogen chloride and potassium hydroxide. Its constitution is now represented by formula II.

(II.)



By the action of ammonia on a methyl-alcoholic solution of the chloride of fluorescein trimethyl ether-ester, Loth (*Diss.*, Lausanne, 1913) has obtained a substance, m. p. 257°, which he considers to be identical with the compound, just mentioned, and to have the following structure:

$$NH\left[CO\cdot C_6H_4\cdot C(OMe)<\begin{matrix}C_6H_3(OMe)\\ C_6H_3(OMe)\end{matrix}>O\right]_2.$$

The stability of the author's compound towards alcoholic hydrogen chloride and potassium hydroxide is, however, not in agreement with this formula. It is possible that both substances are formed in the action of ammonia on the chloride, but that the particular compound isolated depends on the conditions under which the reaction is carried out and the method of working up the product.

In agreement with this view, the author finds that the action of ammonia on the product formed from ethyl sulphate and the disodium salt of fluorescein gives rise to two substances of m. p. 234° and 221°. The former compound has been described previously (this vol., i, 80) as a diethyl ether of fluorescein, but is now considered to have a similar structure to that of the methyl compound represented in II, whilst the second *compound*, m. p. 221°, is presumably the ethyl analogue of Loth's compound.

When heated with acetic anhydride and sodium acetate, and the product treated with water, the chloride of fluorescein trimethyl ether-ester is partly converted into fluorescein dimethyl ether, of m. p. 198°. The dichloride of resorcinolbenzein dimethyl ether, when subjected to

same treatment, yields an *acetyl* derivative, $OAc\cdot CPh<^{C_6H_3(OMe)}_{C_6H_3(OMe)}>O$, crystallising with benzene (1 mol.) in slender, colourless leaflets, which melt and lose their benzene at 110°, then solidify, and have m. p. 178°. This is converted by prolonged boiling with ethyl alcohol into the ethyl ether of m. p. 158°, the acetyl group being replaced by ethyl.

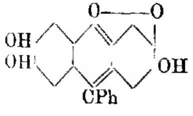
When shaken with ether and ammonia, the dichloride of resorcinolbenzein dimethyl ether yields a *substance*, which forms pale yellow crystals, m. p. 112—113°, and has the following structure:

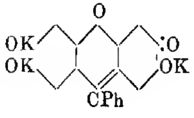
$$OH\cdot CPh<^{C_6H_3(OMe)}_{C_6H_3(OMe)}>NH.$$

Evidence of the existence of eosin in various forms, corresponding with those of fluorescein (A., 1912, i, 379), has been obtained as follows: The chloride, formed by treating fluorescein with a hot mixture of alcohol and hydrochloric acid, is brominated in alcoholic solution and the resulting eosin fractionally extracted with methyl alcohol. The first extractions deposit a dark red eosin, the later fractions a reddish-white or flesh-coloured modification, whilst the residue is either reddish-white or orange. When heated, the eosin from the later fractions acquires a red colour at 200°, then becomes almost white at a temperature below 300°, and finally turns red again and melt at 304—305°. On crystallisation from benzene, the light-coloured eosin separates as a mixture of colourless, yellow and red prisms. The red variety probably corresponds with the red multimolecular modification of fluorescein, the light-coloured form to the yellow unimolecular fluorescein, and the colourless variety to the lactone-form.

When boiled with aqueous alcoholic potassium hydroxide, the light-coloured eosin yields intensely violet or blue solutions. The addition of sulphuric acid to these solutions precipitates a brown substance, which on extraction with boiling chloroform leaves an eosin of the composition $2C_{20}H_8O_5Br_4,CHCl_3$ as a reddish or bluish-white, crystalline residue. The latter compound differs from ordinary eosin in giving a deep violet coloration with strong sulphuric acid, and in yielding with aqueous alkalis deep blue solutions having a green fluorescence; when kept, the blue solutions slowly become violet and finally red. It loses its chloroform at 185—186°, and then dissolves in alkalis with a red colour. Attempts to isolate the blue salt formed by warming the compound with 33% aqueous potassium hydroxide were unsuccessful; instead of the blue salt a brownish-red *tripotassium* salt, $C_{20}H_5O_5Br_4K_3$, was obtained.

Hydroxyquinolbenzein, to which Kehrmann has assigned formula III, yields with aqueous alcoholic potassium hydroxide a *tripotassium* salt IV, which separates in brownish-red crystals of the composition $C_{19}H_{10}O_5K_3,EtOH,H_2O$.

(III.) 

(IV.) 

The author considers that the constitution of hydroxyquinolbenzein is best represented by a quinonoid structure, similar to that given above for the potassium salt, and thus avoids the assumption that the betaine-linking is stable towards alkalis, or that transformation into the quinonoid form occurs. F. B.

Oxidation with Oxygen in Presence of Metallic Osmium. I. RICHARD WILLSTÄTTER and EUGEN SONNENFELD (*Ber.*, 1913, **46**, 2952—2958).—Unsaturated substances alone or diluted with acetone are agitated in special flasks with a small quantity of metallic osmium, prepared by igniting osmium ammonium chloride in a current of hydrogen, in an atmosphere of oxygen. The other metals of the platinum group do not act as oxygen-carriers under these conditions, but tellurium is active, although less so than osmium. A detailed account of the oxidation of *cyclo*hexene by this method is given; the products are Δ^2-*cyclo*hexenol, Δ^1-*cyclo*pentenealdehyde, much adipic acid, and a little adipoin (*cyclo*hexan-2-ol-1-one).

The first two were separated by converting the *cyclo*hexenol into the *naphthylurethane*, m. p. 156°, which crystallises in needles from alcohol or ethyl acetate on cooling its solution in either. Adipoin gives a p-*nitrophenylhydrazone*, m. p. 146° (decomp.), which crystallises from boiling alcohol in orange-red, hexagonal leaflets. T. A. H.

Action of Light on the Colour Changes of Aldehyde Phenylhydrazone Solutions. HANS STOBBE and ROBERT NOWAK (*Ber.*, 1913, **46**, 2887—2902).—The change of colour of solutions of the phenylhydrazones of benzaldehyde, cuminaldehyde, anisaldehyde, piperonaldehyde, and acetaldehyde on exposure to light has been investigated. In all cases the change is extremely sensitive to the action of light. Acid solutions are much more quickly affected than neutral solutions. The change is not due, as supposed by Baly and Tuck (T., 1907, **91**, 1572), to photo-isomerisation of the hydrazones to azo-compounds, but it is an oxidation process which takes place slowly in the dark and is greatly accelerated by light. The colour changes of other hydrazones and of osazones is likewise attributed to oxidation.

Benzaldehydephenylhydrazone is oxidised to dibenzylidenediphenylhydrotetrazone, whilst in no case were azo-compounds formed. E. F. A.

Halogenated Alicyclic Ketones. II. Monohalogenides of Penta-, Hexa-, and Hepta-cyclic Ketones. ARTHUR KÖTZ, K. BLENDERMANN, E. KÁRPÁTI, and RICHARD ROSENBUSCH (*Annalen*, 1913, **400**, 47—54. Compare Kötz and Steinhorst, A., 1911, i, 210).—When *cyclo*pentanone, 1 : 4-dimethyl*cyclo*hexan-3-one, and *cyclo*heptanone are halogenated by Kötz and Götz's method (A., 1908, i, 173), chlorine or bromine is substituted most easily in dimethyl*cyclo*hexanone and least readily in *cyclo*pentanone. The chloro-ketones are stable in the absence of light, but the bromo-ketones decompose very easily. 2-*Chloro*cyclo*pentanone*, b. p. 76—77°, 2-*bromo*cyclo*pentanone*, b. p. 79—82°/15 mm., 2-*chloro*cyclo*heptanone*, b. p. 95°/13 mm., 2-*bromo*cyclo*heptanone*, b. p. 103°/13 mm., and 2-*chloro*-1 : 4-*dimethyl*cyclo*hexan*-3-*one*, b. p. 108—109°/15 mm., are described. C. S.

α-Hydroxy-ketones of the *cyclo*Hexanone and *cyclo*Heptan-[o]ne Series. ARTHUR KÖTZ, K. BLENDERMANN, RICHARD ROSENBUSCH, [an]d E. SIRRINGHAUS (*Annalen*, 1913, **400**, 55—72).—Comparative [e]xperiments on the hydrolysis of 2-chloro*cyclo*pentanone, 2-chloro*cyclo*-[h]exanone, and 2-chloro*cyclo*heptanone by aqueous alkali carbonates [o]r hydrogen carbonates show that *cyclo*pentan-2-olone cannot be [t]hus obtained, that 2-chloro*cyclo*hexanone is readily hydrolysed by [a]queous potassium carbonate in the cold, and that the formation of [c]*yclo*heptan-2-olone in satisfactory yield requires the action of boiling [c]oncentrated potassium carbonate for six hours. *cyclo*Hexan-2-ol-1-one, [m]. p. 98°, forms a *benzoyl* derivative, m. p. 122—123°, *semicarb-[az]one*, m. p. 238°, *oxime*, m. p. 102—103°, *methyl ether*, m. p. 162°, and *ethyl ether*, m. p. 137° (which is converted into the methyl ether by warm methyl alcohol). cyclo*Heptan-2-ol-1-one*, m. p. 28°, unlike *cyclo*hexan-2-ol-1-one, possesses acidic properties and forms a *potassium* derivative. It forms a *methyl ether*, b. p. 65—66°/12 mm., but not a semicarbazone or oxime. The ethers of *cyclo*hexan-2-olone also do not form oximes or semicarbazones, and 2-hydroxy*cyclo*-hexanoneoxime cannot be etherified; the group

OR·CH·C:NOH,

therefore, apparently cannot be formed.

2-Methoxy*cyclo*hexanone does not react with magnesium methyl iodide. *cyclo*Hexan-2-olone reacts only with difficulty, and yields ultimately *cyclo*hexanone (compare Sabatier and Mailhe, A., 1905, i, 706), whilst 1-methyl*cyclo*hexan-3-ol-2-one is similarly converted into 1:2-*dimethyl*cyclo*hexan-3-one*, b. p. 178—179°.

*cyclo*Hexan-2-olone and its methyl and ethyl ethers react with phenylhydrazine in glacial acetic acid to form the same *osazone*, $C_{18}H_{20}N_4$, m. p. 150—151°, red crystals. *cyclo*Hexan-2-olone and its methyl ether are oxidised to adipic acid by alkaline potassium permanganate, and to glutaric acid by boiling nitric acid, D 1·22; the oxidation of the methyl ether is effected much less readily in both cases.

It is well known that hydroaromatic cyclic ketones condense with aldehydes except when a methyl group is present in the ortho-position to the carbonyl group. Hydroxyl and methoxy-groups apparently exert a similar inhibiting influence, because *cyclo*hexanolone or its methyl ether does not condense with benzaldehyde or cinnam-aldehyde in the presence of alcoholic sodium hydroxide. 2-Methoxy-*cyclo*hexanone, however, reacts with sodium and amyl formate in ether to form, after acidification of the product, 2-*methoxy*-6-*hydroxymethyl-ene*cyclo*hexanone*, $C_8H_{12}O_3$, b. p. 98—100°/11 mm. (*semicarbazone*, m. p. 212—215°).

1:4-*Dimethyl*cyclo*hexan-2-ol-3-one*, $C_8H_{14}O_2$, b. p. 91°/13 mm. (*benzoyl* derivative, m. p. 162°), is obtained by boiling 2-chloro-1:4-dimethyl*cyclo*hexan-3-one with saturated aqueous potassium carb-onate, or, in a similar manner, from ethyl 2-chloro-1:4-dimethyl*cyclo*-hexan-3-one-4-carboxylate. Since the last compound, being produced by the chlorination of ethyl 1:4-dimethyl*cyclo*hexan-3-one-4-carboxylate by Kötz and Götz's method, must contain the chlorine atom in position 2 (compare Kötz and Steinhorst, A., 1911, i, 210), it follows, from the

production of 1 : 4-dimethyl*cyclo*hexan-2-ol-3-one by the hydrolysis of both chlorinated substances, that 2-chloro-1 : 4-dimethyl*cyclo*hexan-3-one (preceding abstract) must have this constitution, not that of the 4-chloro-isomeride. The chlorination of ethyl 1-methyl-4-*iso*propyl*cyclo*hexan-3-one-4-carboxylate yields *ethyl 2-chloro-1-methyl-4-*iso*propyl*cyclo*hexan-3-one-4-carboxylate*, by the hydrolysis of which *2-hydroxy-1-methyl-4-*iso*propyl*cyclo*hexan-3-one*, b. p. 139°/17 mm., is obtained.

C. S.

Unsaturated Cyclic Ketones. Δ^2-*cyclo*Hexenone and Δ^2-*cyclo*Heptenone (Tropilene). ARTHUR KÖTZ, K. BLENDERMANN, F. MÄHNERT, and RICHARD ROSENBUSCH (*Annalen*, 1913, **400**, 72—86).—Comparative experiments on the production of unsaturated cyclic ketones from the α-halogenated saturated ketones prove that hydrogen iodide is most readily, and hydrogen chloride is least readily, eliminated, and that the difficulty of eliminating hydrogen haloid increases from halogen-*cyclo*pentanones to halogen-*cyclo*heptanones. Aniline or trimethylamine is the most suitable eliminating reagent; to avoid the formation of hydroxy-ketones, water must not be present.

Willstätter's tropilene is identical with Δ^2-*cyclo*heptenone, obtained by the action of aniline on 2-bromo*cyclo*heptanone; it forms an *oxime*, m. p. 80—88°, and yields *cyclo*heptanone by reduction by Paal's method.

1 : 4-*Dimethyl-Δ^1-*cyclo*hexen-3-one*, $C_8H_{12}O$, b. p. 75°/19 mm., is obtained by heating 2-hydroxy-1 : 4-dimethyl*cyclo*hexan-3-one with anhydrous oxalic acid at 110°. *Ethyl 1 : 2-dimethyl-Δ^1-*cyclo*hexen-3-one-6-carboxylate*, $C_{11}H_{16}O_3$, b. p. 144—146°/13 mm. (*semicarbazone*, m. p. 202°; *oxime*, m. p. 109—110°), obtained by the action of methyl iodide and sodium ethoxide on ethyl 1-methyl-Δ^1-*cyclo*hexen-3-one-6-carboxylate, yields *ethyl 1 : 2-dimethyl*cyclo*hexan-3-one-6-carboxylate*, b. p. 256—258° (*semicarbazone*, m. p. 210—211° [decomp.]), by reduction by Paal's method, and is converted into *1 : 2-dimethyl-Δ^1-*cyclo*hexen-3-one*, b. p. 118—119°/12 mm. (*semicarbazone*, m. p. 225° [decomp.]), by hydrolysis by alcoholic potassium hydroxide and distillation in a vacuum of the resulting acid. 1 : 2-Dimethyl-Δ^1-*cyclo*hexen-3-one is reduced to the corresponding saturated *ketone*, b. p. 84°/11 mm. (*semicarbazone*, m. p. 203—204°), by Paal's method, and yields γ-acetylbutyric acid by oxidation by aqueous potassium permanganate at 0—6°.

C. S.

Zinc Chloride as a Condensing Agent. III. Auto-condensation of Anils. G. REDDELIEN (*Ber.*, 1913, **46**, 2712—2717).—The author has shown previously (A., 1910, i, 118, 746) that acetophenone condenses with aniline in the presence of aniline zincichloride as a catalyst, yielding acetophenoneanil, together with a small quantity of a yellow substance, m. p. 98—99°. The by-product is now found to be dypnoneanil, and is formed by the auto-condensation of acetophenone anil. If the condensation is carried out at 180—190° a better yield of the substance is obtained. It was observed that in all cases in which dypnoneanil was formed as a by-product, the aniline zincichloride used as a catalyst underwent slight decomposition into zinc hydroxide, and

this suggested the possibility that the aniline hydrochloride, simultaneously produced by this decomposition, was the prime factor in the further condensation of acetophenoneanil to dypnoneanil. This view has been confirmed by heating acetophenoneanil for a few minutes with aniline hydrochloride, when a 60% yield of dypnoneanil was obtained; under the same conditions, using aniline zincichloride, the acetophenoneanil remains unchanged.

If the heating is more prolonged and the temperature higher, 1:3:5-triphenylbenzene is formed. Exposure to air at the ordinary temperature also causes the transformation of acetophenoneanil into dypnoneanil, the condensation in this case being probably due to traces of hydrochloric acid in the air, for in closed vessels the acetophenoneanil may be kept for a long time without undergoing change.

Miller and Plöchl (A., 1896, i, 609) have already pointed out that there exists a very close resemblance in the reactions of aldehydes and ketones on the one hand, and of their anils on the other. In emphasising this analogy, the author refers to the similarity in the autocondensation products of acetophenone and its anil, and to the similar behaviour of aldehydes and their anils towards organo-magnesium compounds (Busch, A., 1904, i, 663; 1905, i, 519).

Further, anils closely resemble ketones and aldehydes in their behaviour toward phenylhydrazine and semicarbazide: thus, benzophenoneanil and acetophenoneanil readily react with these compounds in alcoholic solution to form the semicarbazones and phenylhydrazones of the corresponding aldehydes.

Finally, the ability of unsaturated and aromatic aldehydes to form coloured additive compounds with strong acids is shared by anils; fluoroneanil and dypnoneanil yield additive compounds with hydrogen chloride which are coloured respectively red and reddish-yellow, and are rapidly resolved by water into their components.

Dypnoneanil, CMePh:CH·CPh:NPh, forms lustrous, light yellow, glassy prisms, m. p. 98—99°, and gives an intensely yellow coloration with sulphuric acid. It has also been obtained, together with acetophenoneanil, by heating dypnone and aniline in the presence of aniline zincichloride; if aniline hydrochloride is used as a condensing agent, triphenylbenzene is produced.

Dypnone-p-*tolil*, prepared from dypnone and aniline, using *p*-toluidine zincichloride as a catalyst, has m. p. 110°. It is accompanied by acetophenone-*p*-tolil, which crystallises from alcohol in yellowish-white needles, m. p. 31°. F. B.

Catalytic Action of Hydrogen Haloids in Condensations. I. Preparation of Ketoneanils. G. Reddelien (*Ber.*, 1913, **46**, 2718—2723. Compare preceding abstract).—In the preparation of ketoneanils by the condensation of aromatic ketones with amines, hydrogen haloids or their salts with aromatic amines may often be employed as catalysts in place of zinc chloride or amine zincichlorides previously used. Thus, benzophenoneanil is readily obtained by heating benzophenone and aniline at 170° in the presence of one drop of hydrochloric acid.

The reaction proceeds more rapidly than when the zinc salts are

employed, but is not so general in its application. Methyl ketones, such as acetophenone and $\alpha\beta$-unsaturated ketones, do not yield anils by this method, although the latter are readily obtained when aniline zincichloride is employed.

With respect to the mechanism of the reaction the author considers that the ketones first combine with the amines in the presence of hydrochloric acid to form compounds of the type OH·CRR·NHR,HCl, which lose water when heated, yielding hydrochlorides of the anils, CRR:NR,HCl; the anils, however, are very feeble bases in comparison with the amines, and, therefore, are liberated from their hydrochlorides by the action of the unchanged amines, the hydrochlorides of the latter compounds thus being regenerated.

It is pointed out that the hydrogen haloids may act as catalysts in opposite directions accordingly as they ionised or not. Whilst unionised hydrogen haloids act as catalysts in the condensation of ketones with amines, in the ionised state they accelerate the decomposition of the anils into their components and thus exert a catalytic action in the opposite direction.

In addition to benzophenoneanil, the following anils were obtained by heating the necessary ketones and amines in the presence of a little hydrochloric acid: phenyl α-naphthyl-ketoneanil, m. p. 93—94° (compare Busch and Falco, A., 1910, i, 747); benzildianil, m. p. 142°; benzophenone-p-tolil, crystallising from alcohol in long, stout, lustrous prisms, m p. 48° (compare Reddelien, A., 1910, i, 118); benzophenone-α-naphthil (Pauly, this Journ., 1877, ii, 614), which has m. p. 137·5°, and gives a blood-red coloration with strong sulphuric acid; fluorenone-anil (A., 1910, i, 746), the *hydrochloride* of which is precipitated in blood-red needles by passing hydrogen chloride into a benzene solution of the anil. F. B.

Certain Substituted Benzalacetophenones [Phenyl Styryl Ketones]. FRANZ KUNCKELL and MARTIN HAMMERSCHMIDT (*Ber.*, 1913, **46**, 2676—2680. Compare Kunckell and Fürstenberg, A., 1912, i, 118).—2-*Hydroxy*-5-*acetylaminophenyl* 2-*nitrostyryl ketone*, golden-brown needles, m. p. 205° (decomp.), is obtained when aqueous sodium hydroxide is gradually added to an alcoholic solution of 2-hydroxy-5-acetylaminoacetophenone and o-nitrobenzaldehyde and the mixture neutralised after some time with dilute sulphuric acid, the temperature being maintained at about 20° during the whole operation. It is somewhat unstable, and decomposes when preserved for a short time. The preparation of the corresponding dibromide and flavone could not be effected.

2-*Hydroxy*-5-*acetylaminophenyl* 4-*nitrostyryl ketone*,

$$OH·C_6H_3(NHAc)·CO·CH:CH·C_6H_4·NO_2,$$

red, microcrystalline powder, m. p. 204°, is prepared in a similar manner from 2-hydroxy-5-acetylaminoacetophenone and p-nitrobenzaldehyde. It absorbs bromine in chloroform solution, yielding the corresponding *dibromide*, yellow needles, m. p. 125°, after previous softening, from which the flavone could not be obtained by the action of alcoholic potassium hydroxide.

2-*Hydroxy*-5-*acetylaminophenyl* 4-*chlorostyryl ketone*, golden needles,

m. p. 171°, and *2-hydroxy-5-acetylaminophenyl 2-hydroxystyryl ketone*, yellow crystals, m. p. 134°, are similarly formed from their components. In these cases, complete condensation can only be effected by heating the mixture on the water-bath. In neither case could the corresponding dibromide be obtained.

2-Hydroxy-5-acetylaminophenyl 4-methylstyryl ketone forms yellowish-white needles, m. p. 185°. It combines with bromine in chloroform solution to yield *2-hydroxy-5-acetylaminophenyl αβ-dibromo-β-p-tolylethyl ketone*, m. p. 162°.

Terephthalaldehyde condenses with 2-*hydroxy-5-acetylaminoacetophenone*, yielding a yellow *substance*, m. p. 217°, the constitution of which has not been definitely determined. H. W.

Metal Ketyls, a Large Class of Substances with Tervalent Carbon. WILHELM SCHLENK and ALEXANDER THAL (*Ber.*, 1913, **46**, 2840—2854. Compare A., 1911, i, 545).—Phenyl diphenylyl ketone was dissolved in dry ether in an atmosphere of nitrogen, and the boiling point of the solution determined. This remained unchanged on the addition of a piece of bright potassium, indicating that potassium phenyl diphenylyl ketone has the formula

$$Ph\cdot C_6H_4\cdot CPh(OK)-.$$

When a suspension of benzpinacone in benzene is mixed with a concentrated, alcoholic sodium ethoxide solution, sodiobenzophenone is formed, as indicated by the unstable, dark blue coloration. The sodium salt of the benzpinacone at first formed is dissociated immediately into the free radicles with a tervalent carbon atom, $CPh_2(ONa)-$. The name metal ketylen is proposed for such compounds containing tervalent carbon.

Special apparatus is described for their filtration, isolation, and for drying them in a current of nitrogen.

The sparingly soluble ketyls cannot be prepared in the manner described, since the surface of the metal becomes coated with a film of insoluble ketyl which prevents further action.

In such cases the ketone (dimethylpyrone) is mixed with the very soluble potassium phenyl diphenylyl ketone, when the insoluble ketyl (red potassiodimethylpyrone) separates out. Ether, benzene or pyridine may be used as solvents, but the two latter are more difficult to remove from the ketyl. Potassium, sodium, and lithium react equally well; magnesium in the form of amalgam also reacts with diaryl ketones.

Potassiodimethylpyrone forms a bright red powder, which oxidises so readily that it glows on exposure to the air.

Potassiochromone yields a deep orange-red product, and contains a further molecule of chromone. It chars on exposure.

Potassioxanthone separates together with a molecule of xanthone as deep blue needles.

Potassio β-benzpinacolin, $CPh_3\cdot CPh\cdot OK-$, forms dark cubic crystals with a brown surface reflex.

Potassiophthalophenone is dark red.

Potassio-N-methylisatin separates in deep blue flakes.

Potassio-O-methylisatin forms a deep violet precipitate.

Potassio-m-*dibenzoylbenzene*, $COPh\cdot C_6H_4\cdot CPh\cdot OK-$, forms a dark red powder.

Potassio-p-*dibenzoylbenzene* forms a additive compound with two molecules of potassium per molecule; a deep red precipitate is formed, and the solution becomes deep red. The alternative ketyl (I) and quinonoid (II) formulæ are considered, but the latter is rejected,

$$-CPh(OK)\cdot C_6H_4\cdot CPh(OK)- \qquad CPh(OK):C_6H_4:CPh(OK)$$
$$\text{(I.)} \qquad\qquad\qquad \text{(II.)}$$

since the compound behaves like the other ketyls and glows on exposure to the air.

Potassiobenzil, $-CPh(OK)\cdot CPh:O$, is obtained as a violet-coloured precipitate.

Potassiofuril is a black or bluish-black substance.

Potassiophenanthraquinone, $C_6H_4<^{CO-}_{C_6H_4}>C(OK)-$, is dark brown.

Potassio-p-*benzoquinone* possesses a quinhydrone structure combining with a molecule of quinone; it forms a deep bluish-green compound.

When o-benzoquinone is mixed with potassium phenyl diphenylyl ketyl, a dark green precipitate is formed, which soon becomes colourless, and is then potassiocatechol. When the ketyl solution is added slowly to the quinone, a precipitate is formed, and the solution becomes an intense reddish-violet; this is attributed to the formation of the metal ketyl.

On adding diphenyl ketone to the potassium phenyl diphenylyl ketyl an intense violet-red coloration is produced. Excess of the ketyl causes a separation of a compound containing 1 atom of potassium to 2 molecules of diphenyl ketone. The red compound could not be isolated; it possibly has the composition $CPh_2:C(OK)-$.

The atomic groups OK, ONa are considered to exhaust practically the entire valency force of the atoms to which they are attached.

E. F. A.

Preparation of Arylidoquinones. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 262180).—*Di*-p-*chloroanilinobenzoquinone*, a yellowish-brown powder, m. p. over 300°, is obtained by heating together quinol and *p*-chloroaniline in the presence of ammoniacal copper oxide.

Bromoanilinonaphthaquinone is prepared in a similar manner from *p*-bromoaniline and *a*-naphthaquinone. F. M. G. M.

Preparation of 1:4-Diaminoanthraquinone and its Derivatives, or of Sulphonic Acids of these Compounds. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 260899. Compare A., 1901, i, 512; 1905, i, 447; 1909, i, 243).—The preparation of aminoanthraquinones from aminobenzoyl-*o*-benzoic acids has previously been recorded, aud that of 1:4-diaminoanthraquinones from 2-amino-5-acetylaminobenzoyl-*o*-benzoic acid, or its lactam (this vol., i, 621), is now described; the operation is carried out at 190—200° with either 95% or fuming sulphuric acid; under the latter conditions, especially in the presence of boric acid, sulphonated products are also formed. 2:5-*Diaminobenzoyl*-o-*benzoic acid*, yellow

crusts, which melt at 185° with conversion into the *lactam*, can also be employed in this reaction.

1 : 4-*Diamino-2-methylanthraquinone*, dark violet, glistening, bronze needles, m. p. 252°, is obtained from 2 : 5-diamino-*p*-toluoyl-*o*-benzoic acid, whilst 4-chloro-2-amino-5-acetylaminobenzoylbenzoic acid gives rise to 2-*chloro*-1 : 4-*diaminoanthraquinone*, dark violet needles, m. p. 231°.

F. M. G. M.

Replacement of the Sulphonic Acid Group by Halogens in Hydroxyanthraquinonesulphonic Acids. GUSTAV HELLER [with SIEGFRIED SKRAUP (*Ber.*, 1913, **46**, 2703—2711).—Kelbe's method (A., 1883, 806 ; compare also Ullmann and Ochsner, A., 1911, i, 489, and Schilling, this vol., i, 493) of replacing the sulphonic acid group by chlorine or bromine, by the action of these elements on sulphonic acids in aqueous solution, has been applied by the author to the preparation of halogen derivatives of alizarin and anthrachrysone from the corresponding sulphonic acids.

3-Bromo-1 : 2-dihydroxyanthraquinone (D.R.-P. 77179 and 78643) is obtained in a pure condition by the addition of an aqueous solution of potassium bromide and bromate to sodium alizarin-3-sulphonate, acidified with sulphuric acid, and maintained at 95°. It crystallises in rosettes of brownish-red needles, m. p. 260—261°, yields a pale yellow *diacetyl* derivative, m. p. 204—205°, and dissolves in dilute aqueous alkali hydroxides, yielding bluish-violet solutions; concentrated solutions of the hydroxides precipitate the corresponding alkali salts.

3-Chloro-1 : 2-dihydroxyanthraquinone, prepared by passing chlorine into a hot aqueous solution of alizarin-3-sulphonic acid, has m. p. 270—271°, and on benzoylation in pyridine solution yields a *dibenzoyl* derivative, m. p. 184°, together with a red *substance*, m. p. above 300°.

When dissolved in an ice-cold mixture of sulphuric and nitric acids, it is oxidised to 3-*chloro*-1 : 2 : 4-*trihydroxyanthraquinone*, m. p. 242—244°.

Nitration in glacial acetic acid solution yields 3-*chloro*-4-*nitro*-1 : 2-*dihydroxyanthraquinone*. This crystallises in orange-yellow needles, which become dark red and decompose slightly at 220°, then acquire a lighter colour, and finally melt at 285°.

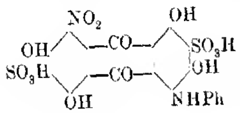
3-*Chloro*-4-*anilino*-1 : 2-*dihydroxyanthraquinone*, prepared by heating the preceding nitro-compound in aqueous sodium carbonate solution with aniline, crystallises in black needles or plates, m. p. 223—224°.

A solution of anthrachrysone in 33% aqueous sodium hydroxide deposits a lustrous, vivid red *sodium* salt, which is converted by ammonium chloride into the *ammonium* salt.

1 : 3 : 5 : 7-Tetrahydroxyanthraquinone-2 : 6-disulphonic acid, prepared by heating anthrachrysone with an excess of fuming sulphuric acid, forms a *sodium* salt, $C_{14}H_6O_6(SO_3Na)_2$, crystallising in glistening, coppery platelets (compare D.R.-P. 70803). On treatment with bromine in dilute acetic acid solution, the sodium salt is converted into 2 : 4 : 6 : 8-tetrabromo-1 : 3 : 5 : 7-tetrahydroxyanthraquinone, which forms lustrous, dark red needles, m. p. above 300°, and yields a sparingly soluble *ammonium* salt.

2 : 6-*Dibromo*-1 : 3 : 5 : 7-*tetrahydroxyanthraquinone*, prepared by brominating anthrachrysone in glacial acetic acid solution, crystallises in orange-red needles, m. p. above 290°, and also forms a sparingly soluble *ammonium* salt.

2 : 6-*Dichloro*-1 : 3 : 5 : 7-*tetrahydroxyanthraquinone* is obtained in lustrous, orange, silky needles by the addition of sodium hypochlorite to an aqueous solution of the sodium salt of anthrachrysone. The action of chlorine on 1 : 3 : 5 : 7-tetrahydroxyanthraquinone-2 : 6-disulphonic acid yields 4 : 8-*dichloro*-1 : 3 : 5 : 7-*tetrahydroxyanthraquinone*-2 : 6-*disulphonic acid*.



8-*Nitro*-4-*anilino*-1 : 3 : 5 : 7-*tetrahydroxyanthraquinone*-2 : 6-*disulphonic acid* (annexed formula) is obtained in the form of its *trisodium* salt (dark bluish-violet crystals of a coppery lustre) by heating a solution of 4 : 8-dinitro-1 : 3 : 5 : 7-tetrahydroxyanthraquinone in aqueous sodium carbonate with aniline.

A similar replacement of the nitro-group by the aniline residue occurs when 4 : 8-dinitro-1 : 3 : 5 : 7-tetrahydroxyanthraquinone (D.R.-P. 71964) is heated with aqueous sodium carbonate and aniline. The 8-*nitro*-4-*anilino*-1 : 3 : 5 : 7-*tetrahydroxyanthraquinone* thus formed crystallises in blackish-blue needles of a coppery lustre.

An account of the tinctorial properties of the above dyes is given.

F. B.

Preparation of a Menthol Ester. ROBERT MEYER (D.R.-P. 261228).—*Menthylglycine hydrochloride*, slender needles, is obtained when a fused suspension of glycine (20 parts) in menthol (70 parts) is treated with continual agitation at about 100° with dry hydrogen chloride and the product purified by crystallisation from water; the free *base*, an oil, is decomposed by warm alkaline hydroxides, and with mercuric chloride furnishes a sparingly soluble *mercury* derivative.

F. M. G. M.

Scission of Racemic Amino-acids by means of Active Acids. I. AMEDEO COLOMBANO and GIUSEPPE SANNA (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 234—237).—A solution containing equimolecular quantities of *d*-camphorsulphonic acid and glycine deposits a salt, $C_{12}H_{21}O_6NS$, which forms long, hygroscopic prisms, m. p. 165—173°, $[\alpha]_D + 14{\cdot}69°$ (in 10·664% aqueous solution). Alanine similarly yields a camphorsulphonate, m. p. 105—110°, $[\alpha]_D^{18} + 14{\cdot}33°$ (in 12·153% aqueous solution). These salts, however, yield racemic products when they are decomposed. Similar results were obtained under many different conditions, and no better success was obtained by substituting *d*-bromocamphorsulphonic acid.

Racemic salts were also produced from leucine and tyrosine in the same way.

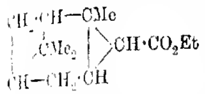
R. V. S.

***dl*-α-Pinene and Ethyl Diazoacetate.** EDUARD BUCHNER and KURT REHORST (*Ber.*, 1913, **46**, 2680, 2687. Compare Buchner and Weigand, this vol., i, 376—387).—The application of ethyl diazo-

acetate to the study of the constitution of *dl*-pinene leads the authors to the conclusion that the latter contains an endocyclic double bond and a methyl group directly attached to a carbon atom having a double bond. This is in conformity with Wagner's formula for pinene.

Pure *dl*-pinene was prepared from American turpentine by subjecting the latter to the action of nitrosyl chloride, the product formed being subsequently decomposed by boiling aniline.

A solution of ethyl diazoacetate in a little *dl*-pinene is slowly added to a mixture of the latter substance and copper powder at 160—165°; nitrogen is violently evolved, and, on distillation, *ethyl* 1:6:6-*trimethyl*-[0,1,$4^{6,7}$,1]-*tricyclooctane-2-carboxylate* (annexed formula), b. p. 135°/12·5 mm., is obtained. Since, however, when suspended in alkali it immediately decolorises permanganate, it is probably contaminated with ethyl fumarate. When saponified with methyl-alcoholic potassium hydroxide, it yields 1:6:6-*trimethyl*-[0,1,4,^{6,7},1]-*tricyclooctane-2-carboxylic acid*, crystalline powder, m. p. 165°, which is stable towards permanganate. The *silver* and *barium* salts were prepared, the latter being readily soluble in water. The *amide*, colourless leaflets, has m. p. 181°. Oxidation by potassium permanganate in hot acid solution converts the acid into a mixture of products from which terebic acid, m. p. 175°, separates after some time. Two other acids can be separated from the residue by converting them into their methyl esters. One of these crystallises in large prisms, whereas the other remains liquid. The latter, when saponified, yields an *acid*, m. p. 211—212°, which could not be further identified on account of its small amount. The former gives methyl*cyclo*propane-1:2:3-tricarboxylic acid, which has m. p. 192°, and does not evolve carbon dioxide at 220°. The identity of this substance is further established by comparison of its methyl ester, m. p. 76·5°, with a synthetically prepared specimen of the same substance (Buchner and Dessauer, A., 1894, i, 347).



The action of ethyl diazoacetate on pinene in the presence of copper powder has been previously investigated by Loose (A., 1909, i, 463), who obtained an oily product which, on saponification, yielded a non-crystallisable substance. This result is attributed to lack of uniformity in the pinene.

The authors have also studied the action of ethyl diazoacetate on *d*-pinene (a_D + 39·8° in 1-dcm. tube) and have obtained a product which, when saponified, yields an acid, colourless needles, m. p. 123°, together with very small quantities of an isomeric acid, m. p. about 165°. With *l*-pinene (a_D − 31·1° in 1-dcm. tube), on the other hand, the main product is the acid, m. p. about 165°, whilst only small amounts of the substance, m. p. about 123°, are obtained. The complete separation of the two acids is difficult, and it is suggested that the acid, $C_{12}H_{18}O_2$, m. p. 123°, is derived from nopinene present in crude optically-active oil of turpentine. H. W.

Bornylene Ozonide. CARL HARRIES and REINHOLD HAARMANN (*Ber.*, 1913, 46, 2595—2596).—By the action of washed, 8% ozone on

bornylene in hexane solution, the *ozonide*, $C_{10}H_{16}O_3$, was obtained as a white precipitate, which gradually decomposed after some time, but was fairly stable towards boiling water. In order to hydrolyse the product, bornylene was saturated with ozone in glacial acetic acid and the solution heated for thirty minutes. The solvent was then evaporated under reduced pressure and the residue distilled, when a pale yellow oil, containing a dialdehyde, b. p. 90—110°/16 mm., and a solid, b. p. 125—150°/18 mm., containing in all probability an aldehydic acid, were obtained. J. C. W.

Research on the Eucalypts of Tasmania and their Essential Oils. RICHARD T. BAKER and HENRY G. SMITH (*Reprint* from the *Proc. Roy. Soc. Tasmania*).—Oils distilled from leaves of the various species of eucalyptus occurring in Tasmania have been examined with a view to ascertain their composition and economic value, and of using some of the data thus obtained as a guide in deciding certain outstanding taxonomic problems in connexion with the genus. The results show that the twenty-one species found in Tasmania may be divided into groups as follows:

I. Eight species yielding oils containing over 50% cineole, much pinene, but no phellandrene or piperitone. The characters of the oils from these species are as follows: ***Eucalyptus cordata***, D_{15}^{15} 0·9138, α_D +9·3°, n_D^{16} 1·4965, saponification number 14·8, soluble in 1·25 vols. of 70% alcohol; contains cineole 62%, *d*-pinene, and esters. *E. Muelleri*, D_{15}^{15} 0·9096, α_D +10·4°, n_D^{24} 1·4629, saponification number 15·3, soluble in 4 vols. of 70% alcohol; contains cineole 60%, *d*-pinene, and esters. *E. Perriniana*, D_{15}^{16} 0·9119, α_D +8·9°, n_D^{15} 1·4651, saponification number 10·3, soluble in 2 vols. of 70% alcohol; contains cineole 68%, *d*-pinene, esters, and sesquiterpene. *E. Rodwayi*, D_{15}^{15} 0·9075, α_D +10·6°, n_D^{23} 1·4653, saponification number 3·9, soluble in 6 vols. of 70% alcohol; contains cineole 64%, *d*-pinene, and sesquiterpene. *E. unialata*, D_{15}^{15} 0·9179, α_D +3·1°, n_D^{15} 1·4690, saponification number 11·1, soluble in 1·75 vols. of 70% alcohol; contains cineole 62%, *d*-pinene, esters, and sesquiterpene. *E. urnigera*, D_{15}^{15} 0·9088, α_D +11·8°, n_D^{21} 1·4638, soluble in 5 vols. of 70% alcohol; contains cineole 63%, *d*-pinene, and esters. *E. vernicosa*, D_{15}^{15} 0·9038, α_D +11·3°, n_D^{18} 1·4651, saponification number 5·9, soluble in 1 vol. of 80% alcohol; contains cineole 59%, and *d*-pinene. *E. globulus*, as already frequently recorded.

II. Two species yielding oils containing cineole from 25—50%, as well as pinene and phellandrene. *E. Gunnii*, D_{15}^{15} 0·9014, α_D +1·5°, n_D^{18} 1·4752, saponification number 6·7, soluble in 4 vols. of 80% alcohol; contains cineole 41%, *d*-pinene, phellandrene, esters, and sesquiterpene. *E. viminalis*, D_{15}^{15} 0·9154, α_D +4·2°, n_D^{19} 1·4711, saponification number 9·5, soluble in 1 vol. of 80% alcohol; contains 50% cineole, *d*-pinene, phellandrene, esters, and sesquiterpene.

III. Two species yielding oils with over 50% cineole, phellandrene largely replacing pinene, and piperitone being present. *E. linearis*, D_{15}^{15} 0·9096, α_D −10·2°, n_D^{24} 1·4659, saponification number 5·8, soluble in 6 vols. of 70% alcohol; contains cineole 52%, with phellandrene, piperitone, and sesquiterpene. *E. Risdoni*, D_{15}^{15} 0·9045—0·9145, α_D −0·3° to 14·6°, n_D 1·4660 (at 19°) to 1·4733 (at 16°), saponification

number 21·3—27, soluble in 1·25—5 vols. of 70% alcohol; contains cineole 56—58%, phellandrene, piperitone, and esters.

IV. Seven species yielding oils containing much phellandrene, less than 25% of cineole, and having piperitone present. *E. amygdalina*, D^{15}_{15} 0·8668—0·8848, a_D $-59·1°$ to $-75·1°$, n^{15}_D 1·4761—1·4790, saponification number 2·9—3·2, soluble in 7 vols. of 70% alcohol; contains cineole 12—24%, phellandrene, piperitone and sesquiterpene. *E. coccifera*, D^{15}_{15} 0·8810, a_D $-35·8°$, n^{24}_D 1·4831, saponification number 4·9, insoluble in 10 vols. of 80% alcohol; contains cineole less than 5%, phellandrene, piperitone and eudesmol. *E. Delegatensis*, D^{15}_{15} 0·8664, a_D $-48·4°$, n^{21}_D 1·4828, saponification number 3·1, insoluble in 10 vols. of 80% alcohol; contains traces of cineole, and is chiefly composed of phellandrene with some piperitone and sesquiterpene. *E. regnans*, D^{15}_{15} 0·8802—0·8879, a_D $-28·4°$ to 31·1°, n_D 1·4882—1·4901, saponification number 13·2—15·4, soluble in 5 vols. of 80% alcohol; contains phellandrene, eudesmol, piperitone, esters, sesquiterpene and traces of cineole. *E. taeniola*, D^{15}_{15} 0·8864, a_D $-27·6°$, n^{17}_D 1·4872, saponification number 3·2, soluble in 5 vols. of 80% alcohol; contains cineole 7%, phellandrene, piperitone, eudesmol and sesquiterpene. *E. virgata*, D^{15}_{15} 0·8883, a_D $-20·9°$, n^{15}_D 1·4819, saponification number 3·3, soluble in 3 vols. of 80% alcohol; contains cineole 21%, phellandrene, piperitone, eudesmol and sesquiterpene. *E. obliqua*, D^{15}_{15} 0·8836—0·8845, a_D $-24·2°$ to 28·8°, n_D 1·4839 (at 19°) to 1·4852 (at 24°), saponification number 7·2—8·1, soluble in 3—4 vols. of 70% alcohol; contains phellandrene, aromadendral, less than 5% of cineole and no piperitone.

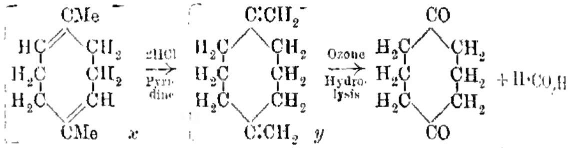
The two remaining species do not fall readily into any of the above groups. *E. acervula*, D^{15}_{15} 0·8956, a_D $-1·1°$, n^{15}_D 1·4756, saponification number 32·8, soluble in 1 vol. of 80% alcohol; contains cineole 21%, *l*-pinene, phellandrene, geraniol, geranyl acetate, liquid and solid paraffins, sesquiterpene. *E. phlebophylla*, D^{15}_{15} 0·8925, a_D $-22·4°$, n_D 1·4761, saponification number 3·2, insoluble in 10 vols. of 80% alcohol; contains cineole 9%, *l*-pinene, phellandrene and eudesmol.

The cineole was determined by the resorcinol method. T. A. H.

The Presence of the 8-Carbon Ring in Normal Caoutchoucs. CARL HARRIES (*Ber.*, 1913, **46**, 2590—2595. Compare this vol., i, 561).—The author has succeeded in degrading Para caoutchouc to *cyclo*octane-1 : 5-dione. The caoutchouc regenerated by heating the dihydrochloride with pyridine (this vol., i, 380) was converted into the diozonide in ethyl acetate solution, and the residue, after removing the solvent under reduced pressure, was heated for an hour with water at 125°. The filtrate was then neutralised with calcium carbonate, filtered, evaporated in a vacuum, and extracted twenty times with ether. The extract was distilled, and the fraction b. p. 60—90°/14 mm. contained chiefly lævulinaldehyde, the fraction b. p. 100—125°/14 mm. partly solidified and contained *cyclo*octane-1 : 5-dione, and the fraction b. p. 180—200°/14 mm. deposited non-aldehydic crystals, m. p. 88°. The syrup of calcium salts was acidified and extracted with ether, and the extract distilled. The products included much formic and lævulic acids and an oily ketonic acid, b. p. 160—180°/14 mm.

The fraction containing *cyclo*octane-1 : 5-dione was redistilled, and the pale yellowish-green distillate, b. p. 107—110°/14 mm., was found to solidify in ice to large, colourless leaflets. It was difficult to remove the last traces of lævulinaldehyde, so the *disemicarbazone*, $C_{10}H_{18}O_2N_6$, was prepared. It forms a white, crystalline mass, m. p. 186·5°.

The variety of products shows that the regenerated caoutchouc consists of a mixture of at least three forms, due to the displacement of the double linkings in the 8-ring, but the formation of so much lævulinaldehyde and acid indicates that a large part of the caoutchouc is regenerated in its natural form. The degradation into *cyclo*butane-1 : 5-dione is represented by the scheme:



J. C. W.

Estimation of Free Sulphur in Vulcanised Caoutchouc. PAUL BARY (*Rev. gen. Chim. pure appl.*, 1913, **16**, 142—145).—Polemical against Alexander (this vol., i, 67), and in agreement with Hinrichsen and Kindischer (A., 1912, i, 706). F. M. G. M.

New Glucosamine Compound and the Constitution of Chitin. YASHIRO KOTAKE and YOSHITA SERA (*Zeitsch. physiol. Chem.*, 1913, **88**, 56—72).—α- and β-Modifications of *lycoperdin*,

$$C_{13}H_{24}O_9N_2,$$

are obtained from the fungus *Lycoperdon gemmatum*. Both show the biuret and iodine reactions and reduce Fehling's solution: they occupy a mean position between the polypeptides and polysaccharides.

α-Lycoperdin is insoluble in water and crystallises in characteristic, granular crystals, $[\alpha]_D$ $-6·7°$, changing to $-5·28°$. It becomes black at 240°. β-Lycoperdin forms a soluble sulphate crystallising in needles.

On hydrolysis, 90% of glucosamine and 14% of formic acid are obtained, equivalent to the formation of two molecules of glucosamine and one molecule of formic acid. Constitutional formulæ are assigned to lycoperdin and to chitin, which is assumed to contain four glucosamine molecules, in all of which the NH_2 group is acetylated. The carbon to which the amino-group is attached is supposed to be directly joined to the potentially aldehydic carbon in the next molecule.

E. F. A.

Application of the Bio-chemical Method to Gentiana acaulis, L. Isolation of a New Glucoside; Gentiacaulin. MARC BRIDEL (*J. Pharm. Chim.*, 1913, [vii], **8**, 241—250).—Investigation of a purified alcoholic extract of *Gentiana acaulis* showed that it contained products hydrolysable by both invertase and emulsin, and in addition a new glucoside, which is not attacked by emulsin, which was isolated and characterised. No gentiopicrin was present.

The new glucoside, ***gentiacaulin***, $C_{47}H_{60}O_{29}$, crystallises from hot alcoholic extracts of the plant in transparent, golden-yellow needles, has no definite melting point, but decomposes from 145° to 160°, and is lævorotatory, $[\alpha]_D$ $-63.84°$ in water. It is precipitated by lead subacetate solution, gives an unstable green coloration with ferric chloride, and reduces Fehling's solution on boiling. It is hydrolysed by boiling dilute sulphuric acid, yielding xylose and *gentiacaulein*, m. p. 177°, crystallising in bright yellow needles, soluble in alcohol or ether, and dissolving in alkalis to give solutions which rapidly become dark brown on exposure to air. T. A. H.

Gitonin, a New Digitalis Glucoside. ADOLF WINDAUS and A. SCHNECKENBURGER (*Ber.*, 1913, **46**, 2628—2633).—Merck's "digitonin" (compare Kiliani, A., 1911, i, 139) is not an individual substance, but contains another glucoside to which the name gitonin is applied. The solubilities of the two substances in alcohol vary considerably with the strength of the solvent. *Gitonin*, $C_{49}H_{80}O_{23}$, is less soluble in 95% alcohol, but more soluble in 85% alcohol, than digitonin, and was obtained in white, amorphous granules when a solution of 100 grams of crude material in 3 litres of 95% alcohol was left for some weeks. It decomposes at 272°, has $[\alpha]_D^{20}$ $-50.69°$, and gives a rose-red to wine-red coloration on boiling with concentrated hydrochloric acid. It forms an *additive* compound, $C_{76}H_{126}O_{24}$, with cholesterol, in sparingly soluble, small, slender needles, and a similar *compound*, $C_{79}H_{130}O_{24}$, with stigmasterol (compare digitonin compounds, A., 1909, i, 172).

After hydrolysis with alcoholic hydrochloric acid, water caused the crystallisation of *gitogenin*, $C_{26}H_{42}O_4$, which was obtained pure after many recrystallisations, in the form of white, narrow leaflets, m. p. 271—272°. It is indifferent towards hydroxylamine, but forms a *diacetyl* derivative, long needles, m. p. 243—244°, a *dipropionyl* derivative, long, narrow leaflets, 195—196°, and yields on oxidation with chromic acid, a dibasic *acid*, $C_{26}H_{40}O_6$, m. p. 242—243°, the *methyl* ester of which crystallises in leaflets, m. p. 145—146°. The sugar syrup did not readily crystallise, although it contained much galactose. The presence, in addition, of 21% of pentoses agrees with the equation: $C_{49}H_{80}O_{23} + 4H_2O = C_{26}H_{42}O_4 + 3C_6H_{12}O_6 + C_5H_{10}O_5$.
J. C. W.

Mustard Oil Glucosides. II. Glucocheirolin. WILHELM SCHNEIDER and LUDWIG A. SCHÜTZ (*Ber.*, 1913, **46**, 2634—2640. Compare A., 1912, i, 1007).—The isolation of the glucoside, glucocheirolin, from wallflower seeds is described. The crude substance was obtained from the dry, fat-free seeds by extraction with several large portions of alcohol which had been dried over sodium. The different fractions contained products in which the proportion, K : S : N, varied, but approached more and more to the expected value 1 : 3 : 1. The very hygroscopic glucoside was then dissolved in water, clarified by shaking with litharge, then quickly treated with lead acetate, and filtered. After precipitating the dissolved lead and exactly neutralising, the solution was concentrated in a vacuum and stirred into absolute alcohol. The precipitate

was then recrystallised a few times from much 90% alcohol, and finally obtained in small, colourless needles, m. p. 158—160°.

Glucocheirolin, $C_{11}H_{20}O_{11}NS_3K,H_2O$, only parts with water after some days in a hot exhausted desiccator over phosphoric oxide. It is tasteless, has $[\alpha]_D^{17}$ $-21.56°$ to $-21.09°$, and gives up one molecule of sulphuric acid on boiling with acidified barium chloride. When silver nitrate is added to the dilute solution, the cheirolin silver sulphate separates after a time as a jelly, in which crystal-centres slowly appear, and finally small, feathery needles, $C_5H_9O_2NS_2,Ag_2SO_4,H_2O$, decomp. 154°, are deposited. The behaviour of glucocheirolin is similar to that of sinigrin and accords with the constitution:

$$SO_2Me\cdot CH_2\cdot CH_2\cdot CH_2\cdot N(O\cdot SO_3K)\cdot S\cdot C_6H_{11}O_5.$$

J. C. W.

Derivatives of α- and β-Bromopicrotoxinins. PAUL HORRMANN (*Ber.*, 1913, **46**, 2793—2801).—The author now finds that picrotoxinin really has the old formula, $C_{15}H_{16}O_6$, not $C_{14}H_{16}O_6$ (A., 1912, i, 709).

By treatment with boiling aqueous potassium hydroxide and subsequent acidification, α-bromopicrotoxinin yields an *acid*,

$$C_{15}H_{17}O_7Br,$$

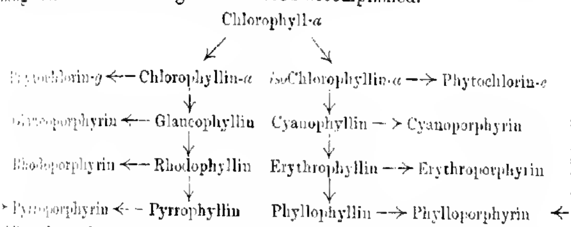
m. p. 248° (decomp.), needles containing H_2O or prisms, $[\alpha]_D^{17.5}$ $-28°51'$ in alcohol ($c = 2.889$) (*methyl* ester, m. p. 218°, $[\alpha]_D^{17.5}$ $-29°21'$; *ethyl* ester, crystals, $[\alpha]_D^{17.5}$ $-31°59'$), a boiling alcoholic solution of which is reduced by zinc dust and aqueous ammonium chloride to *α-picrotoxininic acid*, $C_{15}H_{18}O_7$, m. p. 209° (decomp.), $[\alpha]_D^{17.5}$ $-4°53'$ in alcohol ($c = 5.981$). α-Picrotoxininic acid reacts additively with bromine, reduces alkaline potassium permanganate in the cold and Fehling's solution and ammoniacal silver oxide solution by heating, and neutralises 1 mol. of sodium hydroxide at the ordinary temperature and 2 mols. on the water-bath. It forms a *methyl* ester, m. p. 182°, $[\alpha]_D^{17.5}$ $-9°44'$ in alcohol ($c = 1.970$), and *ethyl* ester, m. p. 159°, $[\alpha]_D^{17.5}$ $-8°4'$ ($c = 4.238$); its potassium salt reacts with aqueous bromine to form an *acid*, $C_{15}H_{17}O_7Br,H_2O$, m. p. 236° (decomp.), $[\alpha]_D^{17.5}$ $-58°2'$ in alcohol ($c = 3.532$). By reduction with palladous chloride and hydrogen at 2 atmospheres, α-picrotoxininic acid yields *α-dihydropicrotoxininic acid*, $C_{15}H_{20}O_7$, m. p. 232° (decomp.), $[\alpha]_D^{17.5}$ $-4°10'$ in alcohol ($c = 2.006$), which is also a lactonic acid, since it neutralises one mol. of alkali in the cold and 2 mol. on the water-bath. By boiling with $2N$-sulphuric acid, α-picrotoxininic acid is converted into an isomeride, *β-picrotoxininic acid*, $C_{15}H_{18}O_7$, m. p. 235° (decomp.), $[\alpha]_D^{17.5}$ $-45°$ in alcohol ($c = 9.254$) (*methyl* ester, m. p. 204°, $[\alpha]_D^{17.5}$ $-50°3'$ in alcohol [$c = 1.049$]; *ethyl* ester, m. p. 198°, $[\alpha]_D^{17.5}$ $-49°57'$ in alcohol [$c = 2.436$]), which is stable to aqueous bromine, does not reduce Fehling's solution or ammoniacal silver oxide solution, and neutralises only 1 mol. of alkali on the water-bath.

C. S.

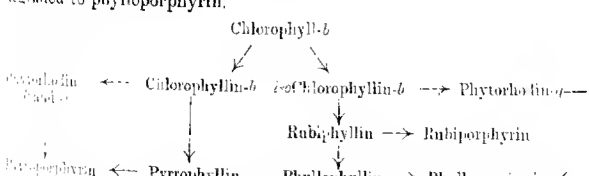
Chlorophyll. XXII. Degradation of the two Components of Chlorophyll by Alkalis. RICHARD WILLSTÄTTER, MAX FISCHER, and LENNART FORSÉN (*Annalen*, 1913, **400**, 147—181. Compare A., 1908, i, 198; 1910, i, 126; 1911, i, 392).—The monocarboxylic acids,

Phyllophyllin and pyrrophyllin, obtained as the final products of the action of alcoholic potassium hydroxide on chlorophyll, are produced, not one from each component of the chlorophyll as might be expected, but both from each component. An explanation of this is to be found in Willstätter and Utzinger's lactam theory of the brown phase (A., [illegible] i, 392). The first action of the alkali on, for example, chlorophyll-*a*, indicated in the colour phase, is rupture of the lactam group and its closure in another direction, yielding chlorophyllin-*a* (lactam group, $\cdot\underset{\gamma}{CO}\cdot\underset{\delta}{NH}\cdot$, closed and the α- and β-carboxyl groups free) and *iso*chlorophyllin *a* (lactam group, $\cdot\underset{\alpha}{CO}\cdot\underset{\delta}{NH}\cdot$, closed and β- and γ-carboxyl groups free); in the subsequent changes caused by the alkali, the lactam groups disappear and the β-carboxyl group is removed, so that the difference between phyllophyllin and pyrrophyllin is due probably to the different positions of the carboxyl groups α and γ.

Rapid hydrolysis of chlorophyll by hot alkalis yields mainly *iso*chlorophyllins *a* and *b* (from which phytochlorin-*e* and phytorhodin-*g* respectively are obtained by eliminating the magnesium by acids); in the cold, the chief products are chlorophyllin-*a* and -*b*, from which phytochlorin-*g* and the feebly basic phytorhodins-*k* and -*i* are respectively obtained by the action of acids. In the *a* series, every change shown in the diagram has been accomplished.



The degradation of chlorophyll-*b* is more difficult, because the second oxygen atom must be reduced without any elimination of carbon dioxide occurring; this has been effected by means of concentrated methyl-alcoholic potassium hydroxide in the presence of pyridine, whereby even the very unstable phytorhodin-*g* has been degraded to phylloporphyrin.



The differentiation and identification of the preceding porphyrins have been effected by the partition method (between hydrochloric acid and ether).

Potassium isochlorophyllin-a, $C_{34}H_{31}O_6N_4MgK_3$, a dark blue powder with a pale green streak, is obtained by boiling gently methylchlorophyllide-*a* with concentrated methyl-alcoholic potassium hydroxide for five minutes and, after further suitable treatment of the solution and dilution with water, adding potassium chloride. Its solutions, in contrast to those of chlorophyllin-*a*, are intensely fluorescent. By heating with pyridine (3 parts) and methyl-alcoholic potassium hydroxide (10 parts) at 150—155° in a silver autoclave for four or five hours, it yields the easily soluble *potassium* salt of the very unstable *cyanophyllin*, $C_{33}H_{34}O_4N_4Mg$. Cyanophyllin is a weaker acid than the isomeric glaucophyllin and is not extracted from ether by 0·003% aqueous ammonia. Its solutions are splendidly blue and intensely fluorescent. By treatment with strong hydrochloric acid it is converted into *cyanoporphyrin*, $C_{33}H_{36}O_4N_4$, reddish-brown needles.

Erythrophyllin, $C_{33}H_{34}O_4N_4Mg$, is prepared from chlorophyll-*a* by boiling with pyridine and methyl alcoholic potassium hydroxide and, after the hydrolysis, heating the alkaline mass in an autoclave at exactly 175—180°; the *potassium* salt, obtained by diluting with water, is then decomposed by sodium dihydrogen phosphate. Erythrophyllin crystallises in pointed rhombic plates, forms a *dimethyl* ester, $C_{35}H_{38}O_4N_4Mg$, long, red prisms, and has weaker acidic properties than rhodophyllin. It is converted into phyllophyllin by methyl-alcoholic potassium hydroxide at 200—210°. Mixtures of cyanophyllin, erythrophyllin, and phyllophyllin can be separated by treating the ethereal solution with 0·2% disodium hydrogen phosphate which extracts the strongest acid, cyanophyllin; somewhat concentrated disodium hydrogen phosphate or not too dilute aqueous ammonia then removes erythrophyllin, the phyllophyllin remaining in the ethereal solution.

Erythroporphyrin, $C_{33}H_{36}O_4N_4$, red, silky prisms, obtained by treating erythrophyllin with concentrated hydrochloric acid and a little ether, forms a *hydrochloride*, pale red needles (insoluble in dilute hydrochloric acid), and a *dimethyl* ester, $C_{35}H_{40}O_4N_4$, brown or reddish-brown prisms, the *hydrochloride* of which is easily soluble in hydrochloric acid.

Di- and mono-basic phyllins derived from the *b* component of chlorophyll are most readily obtained from methylchlorophyllide-*b*. This substance, dissolved in pyridine, is completely hydrolysed by gentle boiling for five minutes with methyl-alcoholic potassium hydroxide, and the blood-red, fluorescent, alkaline solution is heated at 150—155° (whereby an unstable *phyllin* is obtained, the solution of which in ether is green and in alcoholic alkali blue and fluorescent), and finally at 165—170° after dilution with more alcoholic potassium hydroxide. The product is now the *potassium* salt, bluish-violet crystals, of rubiphyllin, from which *rubiphyllin*, $C_{33}H_{34}O_4N_4Mg$, is obtained by treatment with sodium dihydrogen phosphate. Rubiphyllin, which is more easily obtained by hydrolysing methylphæophorbide-*b* or phytorhodin-*g* with methyl-alcoholic potassium hydroxide and heating the resulting solution with magnesium oxide at 170°, crystallises usually in triangular leaflets; its crystalline powder is bluish-black. Rubiphyllin, unlike erythrophyllin and rhodophyllin, is not extracted

from its ethereal solution by 0·5% disodium hydrogen phosphate, but is at once removed by a 1% solution; the *dipotassium* salt,

$$C_{33}H_{32}O_4N_4MgK_2,$$

is a violet powder, which reacts with methyl sulphate to form *rubiphyllin dimethyl* ester, $C_{35}H_{38}O_4N_4Mg$, olive-brown prisms. *Rubiporphyrin*, $C_{33}H_{36}O_4N_4$, obtained by dissolving the preceding potassium salt in 20% hydrochloric acid, crystallises in rhombic leaflets which are olive-brown in transmitted light, and forms a *hydrochloride*, olive-brown prisms, and *dimethyl* ester, $C_{35}H_{40}O_4N_4$, violet prisms.

By heating with methyl-alcoholic potassium hydroxide above 170°, rubiphyllin is converted into phyllophyllin, which is identified as the characteristic calcium salt.

By hydrolysing a pyridine solution of methylchlorophyllide-*b* with methyl-alcoholic potassium hydroxide in the cold, chlorophyllin-*b* is obtained, but always accompanied with *iso*chlorophyllin-*b*; consequently, the degradation products of the former are always contaminated with the phyllins of the *iso*-series, the final products at 205—210° being pyrrophyllin and phyllophyllin. Pure pyrrophyllin can be obtained by hydrolysing methylphæophorbide-*b* by methyl-alcoholic potassium hydroxide in the cold, and heating the resulting alkaline solution with magnesium oxide in a silver autoclave; up to 200°, several still unknown phyllins are formed, but after heating for five hours at 220°, the product is pyrrophyllin, which is identified by conversion into pyrroporphyrin. The latter is obtained directly when phytorhodins-*i* and -*k* are heated at 205—210° with methyl-alcoholic potassium hydroxide alone.

Phytorhodins-i and -k, the latter usually predominating, are obtained together by several methods; the hydrochloric acid number of *k* is 14—14·5, of *i* 15—16, so that their separation requires very careful fractionation with 14% hydrochloric acid. The best method of preparing them is as follows. Chlorophyll (from stinging-nettle leaves) is kept in petroleum for a few weeks until allomerisation is complete. The solution is shaken with concentrated methyl-alcoholic potassium hydroxide until the hydrolysis of the chlorophyll is complete, and then with hydrochloric acid to remove the magnesium. The products are dissolved in ether, the more basic constituents are removed by repeated extraction with 13% hydrochloric acid, and finally the brown ethereal solution is treated with 14—14·5% hydrochloric acid to remove phytorhodin-*k*, and with 17% hydrochloric acid to separate phytorhodin-*i*; the substances require still further purification.

Phytorhodin-k, $C_{34}H_{34}O_6N_4$, black, metallic leaflets, and *phytorhodin*-i, $C_{34}H_{34}O_6N_4$, black, metallic leaflets, resemble one another in their solubilities, but give different colour reactions with potassium hydroxide, cæsium hydroxide, formic acid, and concentrated nitric acid.

By the term "hydrochloric acid" number of a chlorophyll derivative, the author denotes the percentage strength of the hydrochloric acid which is required to extract about 2/3 of the solute from the solution of the derivative in a volume of ether equal to that of the hydrochloric acid. A more rigidly defined number, however, is required for the differentiation of substances which have very nearly equal basicities. This is found in the "partition" number, which

represents the percentage amount of a substance extracted under definite conditions from ethereal solution by hydrochloric acid of a definite strength; the conditions are, 3 milligrams of substance, 1 litre of ether, and 100 c.c. of hydrochloric acid, the extraction lasting one minute. The concentration of the acid is either that denoted by the hydrochloric acid number, or, in the comparison of substances of different basicity, any other concentration suitable for the extraction.

The value of the partition number is illustrated by the comparison of phylloporphyrin and pyrroporphyrin; both have hydrochloric acid number 0·5, but the partition number of the former is about 35 and of the latter about 4.

C. S.

Chlorophyll. XXIII. Parent Substances of the Phyllins and Porphyrins. RICHARD WILLSTÄTTER and MAX FISCHER (*Annalen*, 1913, **400**, 182—194).—Since the degradation of hæmin and of chlorophyll yields similar, but not identical, porphyrins, which, however, give identical products by oxidation (A., 1910, i, 499) and by reduction (A., 1912, i, 41), and since the dissimilarity of the porphyrins is possibly conditioned by differences in the position of the carboxyl groups, the elimination of the latter becomes a matter of prime importance. This has been accomplished with the phyllins and porphyrins derived from chlorophyll. The decarboxylation of chlorophyll derivatives by heating with methyl-alcoholic potassium hydroxide in a sealed tube proceeds only as far as the monocarboxylic acid, decomposition then beginning at 250° with the formation of hæmopyrrole and amorphous, brown products. Complete removal of carbon dioxide from the carboxyl groups, however, is effected by heating rapidly and carefully with soda-lime; the yields are small because the product decomposes at temperatures below the temperature of formation. Potassium rhodophyllin is mixed with soda-lime (free from iron), and is heated in small quantities rapidly and carefully by a naked flame until the colour changes suddenly from pale grey to brown. The mass is rapidly cooled, moistened with water, and extracted with warm ether. The ethereal solution is well washed with potassium hydroxide and with 5% hydrochloric acid. After washing finally with dilute ammonia and concentrating the ethereal solution, a *substance*, $C_{31}H_{34}N_4Mg$, m. p. about 205°, bluish-violet crystals, is obtained, which is called *aetiophyllin*, and is the parent of the phyllins. Aetiophyllin forms violet-red, intensely fluorescent solutions, and in ether is remarkably stable to 4—7% hydrochloric acid; in petroleum, however, even 0·05% hydrochloric acid changes the colour of the solution to that of aetioporphyrin.

Porphyrins lose carbon dioxide much less readily than phyllins, so that the best method of preparing aetioporphyrin, the parent of the porphyrins, is by treating an ethereal solution of aetiophyllin with 20% hydrochloric acid, whereby the magnesium is at once replaced by hydrogen. *Aetioporphyrin*, $C_{31}H_{36}N_4$, m. p. about 280°, hydrochloric acid number 3, partition number for 3% hydrochloric acid 40 (compare preceding abstract), is obtained in violet, crystalline crusts, and forms a *styphnate*, $C_{31}H_{36}N_4,C_6H_3O_8N_3$, m. p. 170°, red prisms, by which it is best purified. It also forms a ***hydrochloride***, olive-brown needles,

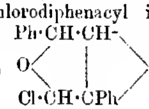
-crate, red prisms, *aurichloride* and *platinichloride*, and yields characteristic complex compounds with salts of the heavy metals.

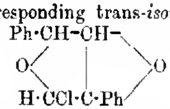
Phylloporphyrin, pyrroporphyrin, and rhodoporphyrin when heated with soda-lime each yields aetioporphyrin, thus confirming Willstätter's theory that the two former are different because of the difference in the position of the carboxyl group.

Aetiophyllin can be obtained from aetioporphyrin by treating a concentrated ethereal solution of the latter with magnesium methyl iodide (Willstätter and Forsén, this vol., i, 499), and subsequently with sodium dihydrogen phosphate.

The absorption spectrum of aetiophyllin is very similar to that of pyrrophyllin, and that of aetioporphyrin to that of pyrroporphyrin, but contains much stronger bands. C. S.

The Quantitative Dyeing of Silk with Basic Dyes. H. Salvaterra (*J. pr. Chem.*, 1913, [ii], 88, 502—504. Compare this vol., ii, 258).—Quantitative experiments on the dyeing of silk with a number of magenta-dyes show that the amount of these dyes taken up by the silk is proportional to their molecular weights, and thus supports the view that the dyeing of silk is a chemical process analogous to salt-formation. F. B.

Constitution of the So-called α- and β-Halogendiphenacyls. Oskar Widman [with G. Karl Almström] (*Annalen*, 1913, 400, 86—130).—The constitutions previously ascribed to the α- and β-halogendiphenacyls (A., 1909, i, 822) are withdrawn and are to be replaced by the following: α-chlorodiphenacyl is cis-2-*chloro*-3:4-oxido-3:5-*diphenyltetrahydrofuran*,  and β-chloro-diphenylacyl is the corresponding trans-*isomeride*,



The evidence on which these constitutions are based is given below the most important proofs being furnished by the reactions of the α- and β-halogendiphenacyls with aniline and with hydrazine hydrate.

Paal and Demeler's statements, that only α-bromodiphenacyl results from the interaction of alcoholic sodium ethoxide and ω-bromoacetophenone and that the α-compound is changed to the β-isomeride by boiling alcohol, are incorrect. The authors show that α-chloro(or bromo-)diphenacyl is unchanged by boiling alcohol, but that in the presence of sodium chloride and a little sodium hydroxide, it is converted almost quantitatively into the β-isomeride in twenty-four to forty-eight hours at the ordinary temperature. In the preparation of the halogendiphenacyls, therefore, both isomerides are formed, the amount of the β-compound being greater the longer the substances are kept in contact with the alcoholic, alkaline mother liquor. Since β-halogendiphenacyl can be converted indirectly into the α-compound (*loc. cit.*), the two compounds are most probably stereoisomeric.

β-Chlorodiphenacyl (*trans*-2-chloro-3 : 4-oxido 3 : 5-diphenyltetrahydrofuran) has m. p. 147—148°, not 154—155°, as stated in the literature.

The course of the reaction whereby ω-halogenacetophenones and alcoholic sodium ethoxide yield oxido-tetrahydrofurans is, in its first stage, probably analogous to those described by Darzens (A., 1905, i, 116) and by Claisen (A., 1905, i, 286), in which ketones or aldehydes condense with esters of halogenated fatty acids in the presence of sodium ethoxide or of sodamide to form esters of substituted glycidic acids: $2CH_2Cl\cdot COPh + NaOH = O<\begin{matrix}CH\cdot COPh\\ CPh\cdot CH_2Cl\end{matrix} + NaCl + H_2O$. The intermediate product then does not yield a four-membered ring by loss of hydrogen chloride, but is converted into a furan derivative, $O<\begin{matrix}CH\cdot CHPh\\ CPh\cdot CHCl\end{matrix}>O$. The two suppositions in this explanation are supported by experimental evidence. With regard to the formation of the oxido-group, the authors find that ω-chloro- or bromo-acetophenone and benzaldehyde in the presence of alcoholic sodium ethoxide, in accordance with Darzen's statement that esters of halogenated fatty acids condense preferentially with aldehydes rather than with ketones, yield not a trace of a furan derivative, but a *substance*, m. p. 89—90°, which proves to be *a-benzoyl-β-phenylethylene oxide*, $O<\begin{matrix}CHPh\\ CH\cdot COPh\end{matrix}$. The second supposition, that a ketone containing a halogen atom in the γ-position to the carbonyl group is capable of yielding a furan derivative, is supported by the behaviour of a substance described by Perkin (T., 1885, **47**, 842) as phenyl ω-bromopropyl ketone; this substance, however, does not exhibit the properties of a ketone, and is most probably 2-bromo-5-phenyltetrahydrofuran.

By heating with a large excess of 99% hydrazine hydrate, α-chlorodiphenacyl (*cis*-2-chloro-3 : 4-oxido-3 : 5-diphenyltetrahydrofuran) is converted into a *substance*, $C_{16}H_{12}N_2$, m. p. 139—140°, faintly yellow, rhombic plates, which proves to be 3 : 5-diphenylpyridazine (Almström, this vol., i, 1240).

By treatment with boiling aniline, α-chlorodiphenacyl yields a *substance* (I.), $C_{22}H_{16}NCl$, m. p. 146—147°, faintly yellow plates, whilst β-chlorodiphenacyl (*trans*-2-chloro-3 : 4-oxido-3 : 5-diphenyltetrahydrofuran) yields a *substance* (II.), $C_{22}H_{17}ON$, m. p. 150°, citron-yellow needles, which forms yellow solutions with bluish-green fluorescence. The constitutions of the substances I. and II. were elucidated after the discovery (compare Almström, *loc. cit.*) that 1 : 3 : 5-triphenylpyrrol-2-one (which is isomeric with II.) is converted by phosphorus trichloride into 2-chloro-1 : 3 : 5-triphenylpyrrole (which is isomeric with I.), and by phosphorus pentachloride into 2 : 4-dichloro-1 : 3 : 5-triphenylpyrrole. Since the last substance is also formed by the action of phosphoric and phosphoryl chlorides on I., it follows that I. must be *4-chloro-1 : 3 : 5-triphenylpyrrole*. Substance II. is then easily proved to be *4-hydroxy-1 : 3 : 5-triphenylpyrrole*, since it forms an *acetyl* derivative, m. p. 132—133°, colourless needles, by treatment with aqueous sodium hydroxide and acetyl chloride in acetone at 0°, and is converted into I. (4-chloro-1 : 3 : 5-triphenylpyrrole) by phosphorus trichloride at 170—190°.

By treatment with warm acetic anhydride and a little concentrated sulphuric acid, 4-hydroxy-1 : 3 : 5-triphenylpyrrole or its acetyl derivative yields *4-acetoxy-2-acetyl-1 : 3 : 5-triphenylpyrrole*,

$$\begin{matrix}OAc\cdot C\text{——}CPh \\ \| \\ CPh\cdot NPh\end{matrix}\!\!>\!C\cdot COMe,$$

m. p. 189—190°, colourless needles, from which *4-hydroxy-2-acetyl-1 : 3 : 5-triphenylpyrrole*, m. p. 180—181°, is obtained by hydrolysis with alcoholic sodium ethoxide.

4-Chloro-1 : 3 : 5-triphenylpyrrole is a very stable substance, and is not attacked by sodium amalgam, boiling alcoholic sodium ethoxide, nitrous acid, or boiling alkaline potassium permanganate. By treatment with boiling acetic anhydride and concentrated sulphuric acid, it yields *4-chloro-2-acetyl-1 : 3 : 5-triphenylpyrrole*, $C_{24}H_{18}ONCl$, m. p. 156° (*semicarbazone*, m. p. about 236° [decomp.]), which reacts with benzaldehyde (1 mol.), 10% sodium hydroxide, and alcohol at the b. p. to form *4-chloro-2-cinnamoyl-1 : 3 : 5-triphenylpyrrole*, $C_{31}H_{22}ONCl$, m. p. 197°, stout, yellow needles. By reduction with hydriodic acid, D 1·22, and amorphous phosphorus at 160°, 4-chloro-1 : 3 : 5-triphenylpyrrole yields 1 : 3 : 5-triphenylpyrrole, m. p. 150—151°, which reacts with boiling acetic anhydride and concentrated sulphuric acid to form *2(?)-acetyl-1 : 3 : 5-triphenylpyrrole*, $C_{24}H_{19}ON$, m. p. 165—166°.

By treatment with methylaniline at 130—140°, α- and β-chlorodiphenacyls yield, not pyrrole derivatives, but phenacylmethylaniline.

Now that the α- and β-halogendiphenacyls have been proved to be *cis*- and *trans*-2-halogen-3 : 4-oxido-3 : 5-diphenyltetrahydrofuran respectively, the nature of their additive compounds with halogen hydrides and acyl haloids (Paal and Stern, A., 1901, i, 154 ; Paal and Schulze, A., 1902, i, 229) is readily understood, and some inaccuracies in the statements of these investigators are easily detected. *trans*-2-Chloro-3 : 4-oxido-3 : 5-diphenyltetrahydrofuran and hydrogen chloride, best in warm glacial acetic acid, yield *2 : 3-dichloro-1-hydroxy-3 : 5-diphenyltetrahydrofuran*, $O\!<\!\begin{matrix}CHPh\cdot CH\cdot OH \\ | \\ CHCl\text{—}CPhCl\end{matrix}$, m. p. 164° (decomp.), which is converted into 4-hydroxy-1 : 3 : 5-triphenylpyrrole and *4-hydroxy-3 : 5-diphenyl-1-p-tolylpyrrole*, m. p. 152°, citron-yellow plates, by aniline and *p*-toluidine respectively on the water-bath. In a similar manner, *trans*-2-chloro-3 : 4-oxido-3 : 5-diphenyltetrahydrofuran and 12% hydrogen bromide in glacial acetic acid at about 30° yield *2-chloro-3-bromo-1-hydroxy-3 : 5-diphenyltetrahydrofuran*, m. p. 155° (decomp.). The substance is given this constitution, not that of the 4-bromo-3-hydroxy-isomeride, because it loses only hydrogen bromide, not both hydrogen chloride and bromide by treatment with alcoholic sodium ethoxide. Contrary to the statement of Paal and his collaborators (*loc. cit.*), the substance, being a bromohydrin, obviously contains a hydroxyl group ; the acetyl derivative, m. p. 89—90°, is obtained by the action of acetic anhydride and two drops of concentrated sulphuric acid. This acetyl derivative is identical with the additive compound (2-chloro-3-bromo-4-acetoxy-3 : 5-diphenyltetrahydrofuran) of β-chlorodiphenacyl and acetyl bromide described by Paal and his co-workers (*loc. cit.*). In a similar manner, the additive compound of β-bromodiphenacyl and hydrogen chloride (*trans*-3-chloro-2-bromo-4-hydroxy-

3 : 5-diphenyltetrahydrofuran) yields an acetyl derivative, m. p. 89—90°, identical with the additive compound of β-bromodiphenacyl and acetyl chloride. Knowing the constitutions of β-chloro- and bromo-diphenacyls, the author is able to assert that the two preceding acetyl derivatives, in spite of their similarities in appearance and m. p., are not identical, as stated by Paal (*loc. cit.*). The assertion is proved, not only by a comparison of the corresponding propionyl and valeryl derivatives which differ in m. p. (see below), but also by the fact that by treatment with alcoholic sodium ethoxide, *trans*-3-chloro-2-bromo-4-acetoxy-3 : 5-diphenyltetrahydrofuran (that is, the additive compound of β-bromodiphenacyl and acetyl chloride) yields *trans*-3-chloro-2-bromo-4-hydroxy-3 : 5-diphenyltetrahydrofuran, whilst *trans*-2-chloro-3-bromo-4-acetoxy-3 : 5-diphenyltetrahydrofuran (the additive compound of β-chlorodiphenacyl and acetyl bromide) is more extensively changed and yields *cis*-2-chloro-3 : 4-oxido-3 : 5-diphenyltetrahydrofuran (α-chlorodiphenacyl). In a similar manner, *trans*-2 : 3-dichloro-4-acetoxy-3 : 5-diphenyltetrahydrofuran, prepared by the addition of acetyl chloride to β-chlorodiphenacyl or by treating *trans*-2 : 3-dichloro-4-hydroxy-3 : 5-diphenyltetrahydrofuran with acetic anhydride and concentrated sulphuric acid, is converted by alcoholic sodium ethoxide into *trans*-2 : 3-dichloro-4-hydroxy-3 : 5-diphenyltetrahydrofuran or *trans*-2-chloro-3 : 4-oxido-3 : 5-diphenyltetrahydrofuran, according as 1 or 2 molecules of the ethoxide are used.

trans-3-Chloro-2-bromo-4-hydroxy-3 : 5-diphenyltetrahydrofuran (the additive compound of β-bromodiphenacyl and hydrogen chloride) yields the *propionyl* derivative, $C_{19}H_{18}O_3ClBr$, m. p. 106°, and the *valeryl* derivative, m. p. 104—105°, by treatment with propionic anhydride and valeric anhydride respectively in the presence of a little concentrated sulphuric acid. By similar treatment, *trans*-2-chloro-3-bromo-4-hydroxy-3 : 5-diphenyltetrahydrofuran (the additive compound of β-chlorodiphenacyl and hydrogen bromide) yields a *propionyl* derivative, m. p. 69°, and *valeryl* derivative, m. p. 93°.

As stated by Paal and Schulze (*loc. cit.*), *cis*-2-halogen-3 : 4-oxido-3 : 5-diphenyltetrahydrofurans (α-halogendiphenacyls) do not react with halogen hydrides to form additive compounds (*cis*-2 : 3-dihalogen-4-hydroxy-3 : 5-diphenyltetrahydrofurans); moreover, these substances cannot be prepared by the action of sodium ethoxide on the *cis*-2 : 3-dihalogen-4-acetoxy-3 : 5-diphenyltetrahydrofurans (additive compounds of α-halogendiphenacyls and acetyl chloride).

Bromodeoxybenzoin, CHBrPh·COPh, and bromopropiophenone, CHBrMe·COPh, by treatment with cold alcoholic sodium ethoxide do not yield analogues of the α- and β-bromophenacyls; the former is converted into the benzoin, m. p. 131°, and the latter into an oily substance which does not contain bromine. C. S.

Conversion of Quinatoxines into Quinaketones and the Reduction of these to the Alkaloids of Cinchona Bark. Adolf Kaufmann and Max Huber (*Ber.*, 1913, **46**, 2913—2924). Rabe and collaborators have shown (A., 1910, i, 417) that of the four asymmetric carbon atoms in the chief cinchona alkaloids, that numbered 3 (*loc. cit.*) is the principal source of the isomerism among the alkaloids,

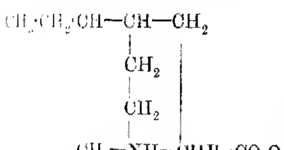
and have explained the apparent formation of a single ketone from each pair of isomerides (A., 1909, i, 252) by assuming that the ketone is tautomeric in each case. They have also shown (Abstr., 1911, i, 742) that cinchotoxine can be converted into cinchoninone and the latter reduced to cinchonine (A., 1908, i, 100), but the yield of the latter is very small, and no proof has been given that it is optically identical with natural cinchonine. The authors now show that in the conversion of cinchotoxine into cinchonine by Rabe's method, the reactions may be regarded as taking place (1) symmetrically, when two pairs of mirror-image isomerides will be formed in equal quantities, or (2) asymmetrically, when 4 optical isomerides will be formed in unequal quantities. They have applied this method to hydrocinchotoxine, and although the results are not conclusive, they indicate that it is the asymmetric direction which the reactions take, whence they conclude that hydrocinchoninone is not an equivalent mixture of two mirror-image isomerides.

Hydrocinchotoxine (hydrocinchonicine), prepared by von Miller and Rohde's method from hydrocinchonine, itself obtained by the reduction of cinchonine by von Skita's process, is an oil having $[\alpha]_D^{21} + 8.8°$ in dry alcohol; it yields a *benzoyl* derivative, m. p. 121—122°, which crystallises from light petroleum in colourless needles, and is sparingly soluble in ether. On treatment in hydrobromic acid with bromine vapour, hydrocinchotoxine yields *bromohydrocinchotoxine dihydrobromide*,

$C_{19}H_{23}ON_2Br,2HBr$,

m. p. 168° (approx.), yellow crystals, readily soluble in water but sparingly so in alcohol, and this with sodium in an alcoholic solution of sodium ethoxide yields hydrocinchoninone, m. p. 130°, which shows mutarotation (compare Rabe, A., 1909, i, 253), and on reduction with palladium black in presence of hydrogen yields dihydrocinchonine (cinchotine), $[\alpha]_D^{21} + 203.4°$, as chief product with a smaller amount of dihydrocinchonidine, m. p. 231°, $[\alpha]_D^{21} - 94.6°$.

In like manner, hydroquinotoxine (hydroquinicine) was converted into *bromohydroquinotoxine dihydrobromide*, $C_{20}H_{25}O_2N_2Br,2HBr,H_2O$, m. p. 178° (annexed formula, in which Q = 6-methoxyquinoline), and this into *hydroquininone*, $C_{20}H_{24}O_2N_2$, m. p. 98—99°, $[\alpha]_D^{21}$, changing from $+83.08°$ after twenty-four hours to $+73.29°$ as the final value, which forms a mixture of needles, platelets, and crusts of yellow colour, and yields a *picrate*, m. p. 224°.



T. A. H.

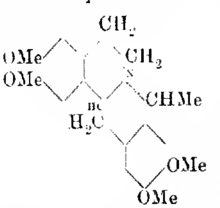
Oxycolchicine. Simon Zeisel and A. Friedrich (*Monatsh*, 1913, 34, 1181—1186).—*Oxycolchicine*, $C_{22}H_{23}(\text{or}_{25})O_7N$, m. p. 266—268°, obtained by oxidising colchicine with potassium pyrochromate and sulphuric acid, crystallises in faintly yellow, microscopic prisms; it is fairly soluble in hot alcohol and readily so in chloroform. Oxycolchicine gives a green colour passing into brown with sulphuric acid,

and with nitric acid a carmine-red changing to violet and brown. With boiling hydrochloric acid it appears to undergo changes quite similar to those given by colchicine. It is insoluble in cold potassium hydroxide solution, but gradually passes into solution on warming, methyl alcohol and acetic acid being split off. Oxycolchicine also reacts with hydroxylamine, but no definite derivative has been obtained. It is probable that in its formation from colchicine a $>CH_2$ group is converted into $>CO$. Formic and acetic acids were found as by-products of the oxidation. Further work on oxycolchicine will be undertaken by Windaus in continuation of his researches on the parent alkaloid (A., 1911, i, 904). T. A. H.

Preparation of Alcoholic Methyl Ethers. J. D. RIEDEL (D.R.-P. 261588).—The following methyl ethers have been prepared from the corresponding alcohols in alkaline solution by means of methyl sulphate: benzyl methyl ether, methyl *iso*amyl ether, and borneol methyl ether; whilst the employment of methyl iodide gave rise to *γ-methylmorphimethine methyl ether*, leaflets, m. p. 259°; *δ-methylmorphimethine methyl ether*, needles, m. p. 277°; *methylcodeine methiodide*, glistening, colourless rods, decomp. 263°; *α-dimethylmorphimethine methiodide*, needles, decomp. 263°; *β-dimethylmorphimethine methiodide*, needles, m. p. 320—330°, and *cinnamyl methyl ether*, b. p. 115°/15 mm. F. M. G. M.

Action of Acetal on Tetrahydropapaverine. AMÉ PICTET and STANISLAS MALINOWSKI (*Ber.*, 1913, **46**, 2688—2697. Compare Pictet and Gams, A., 1911, i, 807).—The authors have studied the condensation of acetal with tetrahydropapaverine, in the hope that it would proceed on similar lines to the action of methylal on veratrylnorhydrohydrastinine, and thus yield one of the optically inactive corydalines. This does not appear to be the case. Two isomeric substances, which the authors name *α*- and *β*-coralydine, are obtained, which have the same composition as the coryladines, but differ from them in their properties.

When acetal is gradually added to a hot solution of tetrahydropapaverine hydrochloride in hydrochloric acid, a mixture of hydrochlorides is obtained, which can be separated by cautious washing with water and subsequent fractional crystallisation from dilute hydrochloric acid. In this manner, *α-coralydine hydrochloride*, m. p. 254°, and *β-coralydine hydrochloride*, m. p. 228—230°, are obtained.



α-Coralydine (annexed formula), prepared by the addition of sodium carbonate to the above hydrochloride, forms colourless, shining leaflets, m. p. 148°. It gives a green coloration with warm, concentrated sulphuric acid. The following salts have been prepared: *sulphate*, m. p. 210°; *nitrate*, m. p. 242°; *picrate*, pale yellow needles, m. p. 134°; *aurichloride*, red crystals, m. p. 154°; *platinichloride*, yellow crystals, m. p. 246—247°. Attempts to resolve the base by quinic acid in alcohol solution and by

d-bromocamphorsulphonic acid in aqueous or alcoholic solution were unsuccessful.

When warmed with alcohol and iodine, α-coralydine yields *dehydrocoralydine*. The *hydriodide*, golden-yellow needles, m. p. 263°; *hydrochloride*, pale yellow needles, m. p. 230°; *nitrate*, yellow needles, m. p. 277—278°, and *aurichloride*, yellowish-brown needles, m. p. 232° (decomp.), of the base have been prepared. These salts differ greatly from the corresponding salts of dehydrocorydaline, from which the conclusion is drawn that the tetrahydro-derivatives, coralydine and corydaline, are structurally isomeric.

Oxidation of α-coralydine by potassium permanganate has been effected according to the directions of Dobbie and Lander for coryladine (T., 1894, 65, 57; 1895, 67, 17). The sole product appears to be m-hemipinic acid, which was identified by conversion into its ethylimide (Goldschmidt, A., 1889, 167). The latter consists of colourless needles (instead of pale yellow needles described by Goldschmidt), m. p. 229°.

β-*Coralydine* crystallises in colourless prisms, m. p. 115°. It gives a colourless solution in cold concentrated sulphuric acid, which becomes green when warmed. Oxidation with alcoholic iodine solution converts it into dehydrocoralydine, the identity of which, with the product obtained in a similar manner from α-coralydine, is established by comparison of the hydrochlorides, hydriodides and nitrates obtained from the two substances. From this it follows that α- and β-coralydines must be stereoisomerides, and probably are related to one another in the same manner as the two inactive corydalines. H. W.

1 Polymeric Tetramethylenecarbamide. 2. Some Derivatives of Pyrrole. EMIL FISCHER (*Ber.*, 1913, 46, 2504—2510).—In attempting to prepare ornithin by the combination of tetramethylenediamine and carbon dioxide, it has been found that the base absorbs carbon dioxide with the formation of a substance which is apparently a carbamate; this, when heated for two days in a sealed tube at 220°, undergoes conversion into a colourless, sparingly soluble compound which commences to decompose at 260°. When heated with lime or in a sealed tube with hydrochloric acid, this substance, which is probably a polymeric form of *tetramethylenecarbamide*,

$$\begin{matrix} CH_2\cdot CH_2\cdot NH \\ | \\ CH_2\cdot CH_2\cdot NH \end{matrix}\!\!>\!CO,$$

regenerates tetramethylenediamine.

Pyrrole-2:5-dicarboxylic acid (Ciamician and Silber, A., 1886, 938) in the form of the sodium salt is easily reduced by sodium amalgam with formation of a *pyrroline-2:5-dicarboxylic acid*, colourless prisms or needles, which becomes pink in the air and when heated commences to decompose at 235°.

2:5-Diacetyl-1-methylpyrrole, m. p. 133—134° (Ciamician and Silber, A., 1887, 843), is more readily obtained by the action of sodium hydroxide and methyl sulphate on 2:5-diacetylpyrrole than by the earlier process starting with 1-methylpyrrole. It can be oxidised by potassium permanganate followed by hydrogen peroxide to 1-*methylpyrrole-2:5-dicarboxylic acid*, needles of no definite m. p.; *silver* salt,

colourless needles. This acid is possibly identical with a substance briefly described earlier (Bell, A., 1879, 525).

Pyrrolealdehyde (Bamberger and Djierdjian, A., 1900, i, 369) can be methylated in alkaline solution by methyl sulphate with production of 1-*methylpyrrole-2-aldehyde*, a colourless oil, b. p. 75—76° (corr.)/12—13 mm., which, unlike the inodorous unsubstituted aldehyde, has an odour resembling benzaldehyde; *phenylhydrazone*, an almost colourless, crystalline powder, m. p. 127—128°(corr.). Oxidation by silver oxide converts the aldehyde into 1-methylpyrrole-2-carboxylic acid, agreeing in m. p. with that described by Bell (*loc. cit.*); *silver* salt, sparingly soluble. D. F. T.

Condensation of Ethyl Oxalate with Acetylpyrroles. OSKAR PILOTY and H. WILL (*Ber.*, 1913, **46**, 2607—2612).—Acetylpyrroles condense with ethyl oxalate with elimination of alcohol, giving rise to coloured compounds which are closely related to the phonopyrrolecarboxylic acids and, therefore, to the blood pigments. The substances are very easily converted into blue, red or green dyes.

3-Acetyl-2 : 4-dimethylpyrrole was condensed with ethyl oxalate in presence of sodium ethoxide, and the product, after evaporating the solvent in vacuum, was acidified with acetic acid, when *ethyl 2 : 4-dimethylpyrryl-3-ethanoneoxalate*, $NH<\begin{matrix}CH{=}CMe \\ CMe{:}C\cdot CO\cdot CH_2\cdot CO\cdot CO_2Et\end{matrix}$ was precipitated. The ester crystallises in lemon-yellow leaflets, m. p. 179·5°, forms a *phenylhydrazone*, $C_{18}H_{21}O_3N_3$, pale yellow, slender needles, m. p. 189°, and yields the *hydrazide* of a *ketazine*, $C_{10}H_{13}ON_5$, in thin, glistening, colourless leaflets, m. p. 235°, when mixed with hydrazine hydrate. When left with 2·5% potassium hydroxide, the ester is hydrolysed to 2 : 4-*dimethylpyrryl-3-ethanoneoxalic acid*,

$$C_{10}H_{11}O_4N,$$

which forms short, golden-yellow, prismatic crystals, decomp. 174°. The ester also dissolves in hot concentrated hydrochloric acid, giving a dark blue solution from which water precipitates the dye in greenish-black masses. On boiling the acid solution for some time, however, the dye separates as an indigo-blue powder. It gives a deep red solution in alkalis.

4-Acetyl-2 : 3-dimethylpyrrole (this vol., i, 196) was also condensed with ethyl oxalate, giving a dark red powder which is insoluble in ether, and also *ethyl 2 : 3-dimethylpyrryl-4-ethanoneoxalate*,

$$NH<\begin{matrix}CMe{:}CMe \\ CH{=}C\cdot CO\cdot CH_2\cdot CO\cdot CO_2Et.\end{matrix}$$

The latter crystallises in long, spindle-like prisms, m. p. 180°, and yields a dark red dye on boiling with concentrated hydrochloric acid. J. C. W.

Electrolytic Oxidation of Cyclic Ammonium Bases. OTTO FISCHER and K. NEUNDLINGER (*Ber.*, 1913, **46**, 2544—2546).—The authors required a convenient method of preparation for 1-methyl-2-pyridone from which a ready passage through the corresponding 2-chloro-compound to the 2-amino-compound is available.

The aim is achieved by electrolytic oxidation of 1-methylpyridinium sulphate between iron electrodes with a catholyte and anolyte of sodium hydroxide solution, the latter (D approx. 1·17) containing also some potassium ferricyanide as catalyst (compare Decker and Kaufmann, A., 1911, i, 1023). The yield of 1-methylpyridone (*picrate*, needles, m. p. 145°) is good, both from the point of view of the substance oxidised and the current passed.

By a similar process, 1-methylquinolinium sulphate can be almost quantitatively converted into 1-methyl-2-quinolone. D. F. T.

Condensation of Unsaturated Aldehydes with Ammonia and Ethyl Acetoacetate. II. E. GRISCHKEVITSCH-TROCHIMOVSKI and (Mlle.) I. PAVLOVSKAJA (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 935—946. Compare A., 1911, i, 320).—Ethyl 2 : 6-dimethyl-4-allyldihydropyridine-3 : 5-dicarboxylate, which exhibits the normal molecular weight in freezing benzene or boiling ether, is converted by oxidation with nitrogen trioxide into *ethyl 2 : 6-dimethyl-4-allylpyridine-3 : 5-dicarboxylate*, $C_{16}H_{21}O_4N$, a yellow liquid, b. p. 208·2°/21 mm., $D_4^{16.5}$ 1·0762, n_D 1·5065; the corresponding *nitrate*, $C_{16}H_{21}O_4N,HNO_3$, m. p. 85·5°, and the *hydriodide*, $C_{16}H_{21}O_4N,HI$, m. p. 137—140° (decomp.), were prepared (see also *loc. cit.*). The free acid, *2 : 6-dimethyl-4-allylpyridine-3 : 5-dicarboxylic acid*, $N{\lessgtr}\genfrac{}{}{0pt}{}{CMe\cdot C(CO_2H)}{CMe{:}C(CO_2H)}{\gtrless}C\cdot CH{:}CHMe$, decomposes at about 205°; its *silver* salt, *hydrochloride*, m. p. about 220° (decomp.), and *platinichloride*, m. p. about 225° (decomp.), were prepared and analysed.

In order to explain the mechanism of the formation of 2 : 4 : 6-trimethylpyridine by the dry distillation of potassium 2 : 6-dimethyl-4-allylpyridine-3 : 5-dicarboxylate (*loc. cit.*), experiments are being made on the condensation of acraldehyde with ethyl acetoacetate and ammonia, which yields *ethyl 2 : 6-dimethyl-4-vinyldihydropyridine-3 : 5-dicarboxylate*, $NH{<}\genfrac{}{}{0pt}{}{CMe{:}C(CO_2Et)}{CMe{:}C(CO_2Et)}{>}CH\cdot CH{:}CH_2$, crystallising in needles, m. p. 86—87°. T. H. P.

The Action of 2-Methylindole on Formic Acid. MAX SCHOLTZ (*Ber.*, 1913, **46**, 2539—2542).—Mainly polemical in favour of the views of the author (this vol., i, 895) and König (A., 1911, i, 809) as opposed to those of Ellinger and Flamand (A., 1911, i, 329) concerning the formula of the product of the interaction of 2-methylindole and formic acid.

The *nitrate* of the substance in question has now been prepared in a similar manner to the method recently described (Scholtz, *loc. cit.*); it forms ruby-red octahedra, decomp. above 220°, the composition agreeing with the formula $C_{19}H_{16}N_2,HNO_3$, or with the less probable $(C_{25}H_{23}N_3)_2,3HNO_3$. D. F. T.

Structure of 3-Nitroso-2-phenylindole. I. and II. LUIGI ALESSANDRI (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 150—155, 227—234. Compare Angeli and Morelli, A., 1908, i, 828).—In this preliminary note the author describes some transformations under-

gone by this substance. The production of the *O*-ether described by Angeli and Spica (A., 1899, i, 938) is confirmed. When nitrosophenylindole is heated, small quantities of 2-benzoylaminobenzonitrile are produced. This compound has m. p. 156°, but is readily converted by dilute acids into the corresponding amide, m. p. 216°. The supposed 2-benzoylaminobenzonitrile of Pinnow and Sämann (A., 1896, i, 365) probably consisted of this amide.

By the action of phosphorus pentachloride, 3-nitroso-2-phenylindole is converted into 2-phenyldihydro-4-quinazolone. When 3-nitroso-2-phenylindole is heated with zinc chloride, an apparently isomeric substance, m. p. about 228°, is formed, together with other products. This substance yields the above-mentioned quinazoline derivative when boiled with dilute acids or alkalis, and the same quinazoline derivative is also produced when the amide of m. p. 216° is heated.

The second paper gives experimental details regarding the results recorded in the first paper. 2-Benzoylaminobenzonitrile, prepared either by heating nitrosophenylindole (*loc. cit.*), or from 2-aminobenzonitrile, crystallises in colourless prisms or in long needles, m. p. 156°. R. V. S.

Scission of Decahydroquinoline into the Two Optical Antipodes. Bruno Veneziani (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 155—157).—Synthetical decahydroquinoline can be resolved with the aid of *d*-bromocamphorsulphonic acid. d-*Decahydroquinoline d-bromocamphorsulphonate* forms acicular crystals, m. p. about 220°, $[\alpha]_D^{22}$ +64·01° (in 1·117% aqueous solution), and is less soluble than the *l*-salt, which was obtained only in the form of an oil. d-*Decahydroquinoline* has $[\alpha]_D^{22}$ +1·28° (in 4·013% ethereal solution). l-*Decahydroquinoline* has $[\alpha]_D^{22}$ −1·02° (in 14·11% ethereal solution). In consequence of the small quantity of substance available, the author suggests that the rotatory powers of the pure enantiomorphs may be numerically greater than those above recorded. R. V. S.

Arsenic Compounds of the Quinoline Group. Sigmund Fränkel and Paul Löwy (*Ber.*, 1913, **46**, 2546—2550).—The authors have turned their attention to the arsenic compounds of quinoline because both constituents of such molecules would be physiologically active.

Schiff (*Annalen*, 1864, **131**, 116) has already given a brief report on certain compounds from quinoline and arsenic trichloride. It is now found that the action of quinoline and analogous bases with arsenic trichloride is an additive one; the action was effected in ethyl acetate solution with equimolecular quantities of the reagents. *Quinoline arsenotrichloride*, $C_9H_7N,AsCl_3$, is a colourless solid, m. p. 138°; *tetrahydroquinoline arsenotrichloride*, $C_9H_{11}N,AsCl_3$, is a pink solid, m. p. 134°; 8-*hydroxyquinoline arsenotrichloride*, $C_9H_7ON,AsCl_3$, is a bright yellow substance, m. p. 168°. Even under the influence of aluminium chloride the arsenic atom could not be made to enter the quinoline nucleus, and a similar failure was experienced when quinoline and tetrahydroquinoline were heated with arsenic acid at 200° in a sealed

tube, the products being *quinoline arsenate*, bright yellow leaflets, decomp. at 250°, and *tetrahydroquinoline arsenate*, colourless leaflets, m. p. 123°.

Attempts to synthesise the quinoline nucleus from arsanilic acid by Skraup's method gave merely quinoline, whilst Knorr's process with ethyl acetoacetate left the arsanilic acid unaltered. However, arsanilic acid condenses with acetaldehyde when an intimate mixture is treated with hydrobromic acid (D 1·49); the *hydrochloride* of 2-*methylquinoline-arsinic acid*, a yellow, crystalline solid, separates, from which the free acid, decomp. at 140°, can be liberated by washing with distilled water. Reduction of this acid in alcohol by sodium yields the tervalent arsenic compound, 2-*methylquinolinearsenoxide*, decomp. at 120°; the *picrate* was prepared. D. F. T.

Synthesis of 2-Cyanoquinoline and 1-Cyano*iso*quinoline. ADOLF KAUFMANN and PAUL DÄNDLIKER (*Ber.*, 1913, **46**, 2924—2929).—2-Cyanoquinoline, already prepared by Pfitzinger (Abstr., 1902, i, 53), was made by treating Reissert's 2-cyano-1-benzoyl-1 : 2-dihydroquinoline, dissolved in chloroform, with phosphorus pentachloride. It is readily hydrolysed to quinaldinic acid, which is also formed as a by-product in the preparation of the cyano-base.

1-*Cyanoisoquinoline*, similarly obtained from 1-cyano-2-benzoyl-1 : 2-dihydro*iso*quinoline (Reissert, Abstr., 1905, i, 926) has m. p. 74°, crystallises from light petroleum, and is very soluble in ether or alcohol, but sparingly in water. On hydrolysis by acids or alkalis, it yields *iso*quinaldinic acid (*iso*quinoline-1-carboxylic acid). T. A. H.

Preparation of Arylquinolinecarboxylic Acid Esters. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 261028).—*Salicyl 2-phenylquinoline-4-carboxylate*, colourless leaflets, m. p. 188°, is obtained when a benzene solution of 2-phenylquinoline-4-carboxylic acid is warmed during two hours with thionyl chloride and the solid residue (left after evaporating the solvent) mixed with salicylic acid and benzene and heated during three hours at 80°.

o-*Hydroxytoluoyl* 2 : 3-*diphenylquinoline*-4-*carboxylate*, colourless needles, m. p. 250°, is prepared in an analogous manner from hydroxytoluic acid and 2 : 3-diphenylquinoline-4-carboxylic acid. *Salicyl* 2-p-*anisylquinoline-4-carboxylate*, colourless needles, has m. p. 132°, and *salicylglycine 2-phenylquinolinecarboxylate*, m. p. 120°. F. M. G. M.

Quinolyl Ketones. III. ADOLF KAUFMANN, PAUL DÄNDLIKER and HANS BURKHARDT (*Ber.*, 1913, **46**, 2929—2935. Compare Abstr., 1912, i, 1017; this vol., i, 294).—It is now shown that in the preparation of these ketones by the use of Grignard reagents with cyanoquinolines, a molecule of the magnesium alkyl iodide is first attached to the cyclic nitrogen and then a second molecule to the cyano-group. The position of the cyano-group has some influence on the reactions; thus 2-cyanoquinoline and 1-cyano*iso*quinoline give good yields of the corresponding alkyl ketones, whilst 5-cyanoquinoline does not react with Grignard reagents.

2-*Quinolyl methyl ketone*, $C_9H_6N\cdot COMe$, m. p. 52°, b. p. 146—148°/

13 mm., forms small needles from dilute alcohol, and has a jasmine-like odour. The *phenylhydrazone*, m. p. 154°, crystallises from alcohol in slender, yellow needles. 2-*Quinolyl ethyl ketone*, m. p. 59—60°, distils in steam, forms colourless needles from alcohol, and has a pleasant ketone-like odour. The *phenylhydrazone*, m. p. 106°, forms short, yellow needles. 2-Quinolyl phenyl ketone was also prepared by this means (compare Besthorn, 1908, i, 681). 2-*Quinolyl benzyl ketone*, m. p. 78°, crystallising in flat needles, was prepared by treating 2-cyanoquinoline with magnesium methyl iodide followed by magnesium benzyl chloride, or by the action of ethyl quinaldinate on the sodium derivative of benzyl cyanide, which gave 2-*quinolyl cyanobenzyl ketone*, m. p. 120—121°, long needles, which was then hydrolysed to the corresponding *acid* and the latter heated at 120—130°.

1-iso*Quinolyl methyl ketone*, m. p. 48°, crystallises in colourless needles, is readily soluble in organic solvents, and has only a slight odour. The *phenylhydrazone* decomposes at 160°. 1-iso*Quinolyl phenyl ketone*, m. p. 76—77°, b. p. 231°/12 mm., crystallises in highly refractive tablets, is readily soluble in benzene, alcohol or ether, but sparingly in light petroleum. It does not yield a methiodide with methyl iodide at 100° under pressure. T. A. H.

New Synthesis of Carbostyril. HANS MEYER and ROBERT BEER (*Monatsh.*, 1913, **34**, 1173—1179).—When *o*-chlorocinnamic acid is heated with copper and ammonia solution it is partly converted into carbostyril (2-hydroxyquinoline), the reaction being almost complete when the mixture is heated during thirty hours at 160—170°. At 120—130°, on the contrary, more or less *o*-aminocinnamic acid is also formed. A process for the isolation of the latter is described. The *o*-aminocinnamic acid produced in this reaction differs in certain respects from that prepared by reduction of *o*-nitrocinnamic acid, being (1) more soluble in water; (2) not readily convertible into coumarin, and (3) of different melting point, namely, 150°. It seems possible that it may be a new *trans*-form of the acid (compare Stoermer and Heymann, Abstr., 1912, i, 974).

When 2-methoxyquinoline is (1) distilled under atmospheric pressure, (2) heated on a water-bath, or (3) kept for some time in diffused light, it passes into the non-volatile isomeride in which the methyl group is attached to the nitrogen, a change analogous with the conversion of α-methoxypyridine into *N*-methylpyridine (compare Abstr., 1901, i, 343).

o-Chlorophenylpropionic acid when heated at 140—160° with copper and ammonia solution during thirty hours is converted quantitatively into hydrocarbostyril. T. A. H.

Nitro-derivatives of Thiodiphenylamine [Phenthiazine]. FRIEDRICH KEHRMANN and OLGA NOSSENKO (*Ber.*, 1913, **46**, 2809—2820).—The nitrophenthiazinesulphoxides obtained by the action of nitric acid on phenthiazine (Bernthsen, A., 1886, 53) are converted into the corresponding nitrophenthiazines by mineral acids in the presence of alcohol or glacial acetic acid; the most suitable reagent is concentrated hydrochloric and glacial acetic

acids, although it has a tendency to replace nitro-groups by chlorine atoms and to form chlorinated products. Smiles and Barnett (T., 1909, 95, 1261) and Claasz (A., 1912, i, 513) have examined the action of such reagents on nitrated phenthiazinesulphoxides and have described the products as derivatives of phenazothionium hydroxide. This is incorrect, the products obtained by these investigators being nitrophenthiazines mixed with chlorinated and oxidised by-products.

5-*Nitrophenthiazine*, $C_6H_4<{NH \atop S}>C_6H_3\cdot NO_2$, m. p. 111°, violet-black leaflets, is obtained by condensing *o*-aminophenyl disulphide with 1-chloro-2:6-dinitrobenzene (2 mols.) in boiling alcohol in the presence of sodium acetate (2 mols.), and reducing the resulting dinitrodiphenylamine disulphide in boiling alcohol and benzene with concentrated aqueous sodium sulphide; the yield is very unsatisfactory. By reduction with stannous chloride and hydrochloric acid, it is converted into 5-*aminophenthiazine hydrochloride*, colourless needles, which is oxidised by aqueous ferric chloride to 5-*aminophenazothionium chloride*, $C_6H_4<{-N- \atop SCl}\geqslant C_6H_3\cdot NH_2$, which is isolated as the *platinichloride*, $2C_{12}H_9N_2SPtCl_6$, greyish-green crystals. 5-Aminophenthiazine forms an *acetyl* derivative, m. p. 174°, colourless prisms.

3-*Nitrophenthiazine*, m. p. 218°, violet-black crystals, is obtained by treating an alcoholic suspension of 3-nitrophenthiazinesulphoxide with 30% sulphuric acid, warming finally on the water-bath. The sulphoxide is converted by hydrochloric and acetic acids into 9(?)-*chloro-3-nitrophenthiazine*, $C_6H_3Cl<{NH \atop S}>C_6H_3\cdot NO_2$, m. p. about 268°, brownish-black, bronze needles; by reduction, the latter yields the chloroaminophenthiazine by the oxidation of which by ferric chloride the chloroaminophenazothionium chloride is obtained.

The action of hydrochloric and acetic acids on 3:9-dinitrophenthiazinesulphoxide yields a mixture of 3:9-dinitrothiodiphenylamine and a *tetrachloro*-derivative, m. p. 235°, colourless needles (probably 3:5:7:9-*tetrachlorophenthiazine*), which is separated by extracting the latter with chloroform. 3:9-*Dinitrophenthiazine*,

$$NO_2\cdot C_6H_3<{NH \atop S}>C_6H_3\cdot NO_2,$$

m. p. 276°, dark brownish-red needles, forms solutions with a characteristic brick-red fluorescence and yields by reduction the leuco-derivative of Lauth's violet. It is also the chief product of the action of solid sodium nitrite on a suspension of phenthiazine in glacial acetic acid.

Smiles and Barnett's tetranitrophenthiazinesulphoxide (*loc. cit.*) is, contrary to their statement, practically unchanged by treatment with alcohol and mineral acids. From the by-products in its preparation a *substance*, $C_{12}H_6O_8N_4S$, m. p. 270°, yellow needles, is obtained, which is probably a *hydroxytrinitrophenthiazinesulphoxide*.

Attention is called to the fact that all nitrophenthiazines containing at least one nitro-group in the para-position to the nuclear nitrogen

atom form intensely blue or green alkali salts, which probably have the quinonoid constitution $C_6H_4<^{N}_{S}>C_6H_3:NO\cdot OM$. C. S.

Preparation of Anthraquinonedithiazoles and their Reduced Derivatives. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 260905).—2 : 6-*Diaminoanthraquinone*-1 : 5-*dimercaptol* is obtained by heating 1 : 5-dichloro-2 : 6-diaminoanthraquinone with an aqueous-alcoholic solution of sodium polysulphide under pressure, and it has been employed in the preparation of the following *compounds*: (1) by boiling the foregoing mercaptol (50 parts) with 50 to 100 parts of either benzaldehyde, benzylidene chloride, benzotrichloride, or benzoyl chloride; (2) in a similar manner with *p*-dimethylaminobenzaldehyde; (3) with anthraquinone-2-aldehyde.

The tinctorial properties of these compounds are described, also modifications in methods of preparation, whilst the same reaction with other aldehydes and mercaptols is also discussed. F. M. G. M.

Quinone-benzidine and its Reaction Products. KURT BRASS (*Ber.*, 1913, **46**, 2902—2906).—When the components are brought together in toluene, 2 mols. of benzidine unite with 1 mol. of quinone to form a soluble bluish-black addition product (compare Fecht, A., 1908, ii, 916). On warming in alcohol, an insoluble brown powder is obtained containing benzidine and quinone in molecular proportions.

The bluish-black product crystallises in platelets, m. p. 118°. The brown product does not melt; it dissolves with a blue coloration in concentrated sulphuric acid, and probably represents a polymeride.

Chloranil and benzidine when warmed together in toluene solution condense to an insoluble brown vat dye, which is regarded as a mixture of dibenzidinodichloroquinone with a little monobenzidinotrichloroquinone. E. F. A.

Oxidation of Anilinoquinones to Benzidine Derivatives. II. KURT BRASS (*Ber.*, 1913, **46**, 2907—2912. Compare A., 1912, i, 874).—1-Anilinoanthraquinone is readily oxidised by manganese dioxide and sulphuric acid to N : N′-bis*anthraquinonyl*-1-*benzidine*, a clear violet vat dye, which is composed of microscopic, transparent, violet crystals, m. p. 311°. The solution in concentrated sulphuric acid is olive-green.

In a similar manner, 1-anthra-anilinoanthraquinone may be oxidised to N : N′-*bis*-(*anthraquinonyl*-1)-*benzidine*-o-*dicarboxylic acid*, which forms a mass of violet-red needles, m. p. about 360°. On heating in concentrated sulphuric acid at 100—110°, the green solution becomes orange, and *dianthraquinone*-2 : 1-*acridone*,

$$C_6H_4<^{CO}_{CO}>C_6H_2<^{CO}_{NH}>C_6H_3\cdot C_6H_3<^{CO}_{NH}>C_6H_2<^{CO}_{CO}>C_6H_4$$

is obtained in the form of a mass of pale violet needles. It does not melt or sublime.

Bis-α-naphthoquinonyl-2-benzidine, obtained on oxidation of anilino-α-naphthoquinone, gives a brownish-violet solution in concentrated sulphuric acid. E. F. A.

Phenylhydrazine. I. Anhydrous Phenylhydrazine as a Cryoscopic Solvent. BERNARDO ODDO (*Gazzetta*, 1913, **43**, ii, 263—274).—The cryoscopic constant of phenylhydrazine is 58·59 (from experiments with naphthalene, diphenyl, dibenzyl, veratrole, and safrole). The molecular weight of hydrocarbons (benzene, toluene, *p*-xylene, and *p*-cymene) dissolved in phenylhydrazine increases with the concentration, and the same phenomenon is observed with alcohols (ethyl alcohol, *iso*butyl alcohol, *iso*amyl alcohol, and ethylene glycol); triphenylcarbinol gives a value below the normal at all concentrations. Phenols (phenol, *p*-cresol, and β-naphthol) have molecular weights below the theoretical value, and they diminish slowly when the concentration is increased. Bases (pyridine, piperidine, aniline, dimethylaniline, and quinoline) behave normally. Acetic acid and butyric acid are almost normal, whilst benzoic acid and salicylic acid have molecular weights much below the calculated values. R. V. S.

Phenylhydrazine. II. The System Phenylhydrazine–Water and the Cryoscopic Constant of Hydrated Phenylhydrazine. BERNARDO ODDO (*Gazzetta*, 1913, **43**, ii, 274—281. Compare preceding abstract).—Phenylhydrazine and phenylhydrazine hydrate show an eutectic point at 16°, and there is a maximum corresponding with the formula $(NHPh{\cdot}NH_2)_2,H_2O$, which agrees with that of the phenylhydrazine hydrate already known. The cryoscopic constant of phenylhydrazine hydrate is 44·15 (from experiments with diphenyl, veratrole, and naphthalene). R. V. S.

Phenylhydrazine. III. Velocity of Reaction of Aldehydes and Ketones with Phenylhydrazine. BERNARDO ODDO (*Gazzetta*, 1913, **43**, ii, 354—362. Compare preceding abstracts).—Comparative cryoscopic experiments show that the reaction of phenylhydrazine with acetone is complete in forty minutes, that with acetophenone in 162 minutes, whilst that with benzophenone has hardly begun after 225 minutes. Tables are also given showing the cryoscopic behaviour of a number of aldehydes and ketones in phenylhydrazine. R. V. S.

Action of Stannic Chloride on Phenylhydrazine. JITENDRA N. RAKSHIT (*J. Proc. Asiatic Soc., Bengal*, 1913, **9**, 131—135, Reprint).—Pure stannic chloride reacts very vigorously with phenylhydrazine, yielding benzene and nitrogen, whilst phenylhydrazine hydrochloride may be isolated from the product by dissolving it in water, precipitating the tin as the sulphide, and concentrating. A quantitative study of the reaction has shown that two molecules of the base give rise to one molecule of benzene, one of phenylhydrazine hydrochloride, and one of nitrogen. The equation:

$$2NHPh{\cdot}NH_2 + SnCl_4 = C_6H_6 + N_2 + SnCl_2 + NHPh{\cdot}NH_2,2HCl$$

agrees with these results, but introduces the anomaly that phenylhydrazine forms a dihydrochloride. Such an easily decomposable compound would be analogous to the dihydrofluoride described by Thieme (A., 1893, i, 155), and since no double salt of the base with a chloride of tin could be detected, its existence must be taken for granted.

The question whether the benzene is formed through the intervention of benzenediazonium chloride remains to be proved.

J. C. W.

Mutual Replacement of Ammonia and Amines in Carbon Compounds. N. Conev and Pavel Iv. Petrenko-Kritschenko (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1092—1098).—In order to throw light on the results obtained by Schöttle and Petrenko-Krittschenko (A., 1911, i, 1020; 1912, i, 128; this vol., i, 48), the authors have investigated the action of ammonia and amines on acetylphenylmethylpyridonone (compare von Pechmann and Neger, A., 1893, i, 398), which differs from benzoyldehydracetic acid in that the two phenyl side-groups are replaced by methyl groups. The substituents have such a considerable influence on the course of the reaction that the latter is of an entirely different character from that previously observed. The ring is here found to exhibit great stability, substitution of oxygen and mutual replacement of ammonia and amines taking place only in the side-chains. Further, heating of acetylphenylmethylpyridonone with hydrochloric acid results in the separation, not of aniline, but of acetic acid.

The action of ammonia on 5-acetyl-1-phenyl-2-methylpyridonone gives a quantitative yield of the *compound*,

$$CMe<\begin{matrix}CH-CO\\NPh\cdot CO\end{matrix}>C:CMe\cdot NH_2,$$

m. p. 247—248°. Similarly, the action of methylamine gives the *compound*, $CMe<\begin{matrix}CH-CO\\NPh\cdot CO\end{matrix}>C:CMe\cdot NHMe$, in colourless, thin needles, m. p. 183°, and that of aniline the *compound*, $C_{12}H_9O_2N:CMe\cdot NHPh$, m. p. 154—155°.

When these derivatives are subjected to suitable conditions, the methylamine or aniline residue may be replaced by the amino-group, the latter by the methylamine or aniline residue, or the aniline by the methylamine group.

1-*Phenyl-2-methylpyridonone*, $NPh<\begin{matrix}CMe:CH\\CO-CH_2\end{matrix}>CO$, obtained by heating the acetyl compound with excess of concentrated hydrochloric acid in a sealed tube at 150°, forms transparent, lustrous plates, m. p. 270—271°, and yields an *acetyl* derivative, $NPh<\begin{matrix}CMe:CH\\CO-CH\end{matrix}>C\cdot OAc$, which crystallises in needles, m. p. 146—147°, and is isomeric with von Pechmann and Neger's compound (*vide supra*). With benzaldehyde, it yields 1-*phenyl-5-benzylidene-2-methylpyridonone*,

$$NPh<\begin{matrix}CMe=\!=\!=CH\\CO\cdot C(:CHPh)\end{matrix}>CO,$$

m. p. 308—309°, which has the normal molecular weight in freezing phenol.

T. H. P.

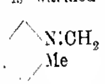
Synthesis of Aminoacetyl-8-methoxyquinoline. Sigmund Fränkel and Oskar Grauer (*Ber.*, 1913, **46**, 2551—2554).—After several fruitless attempts to prepare substances which should constitu-

tionally resemble adrenaline, the authors have obtained the above substance.

8-Methoxyquinoline was prepared by the method of Bedall and Fischer (A., 1882, 412) improved by the replacement of ether by benzene for the purpose of extraction; the base, needles, b. p. 172°/24 mm., gives a *platinichloride*, and a *picrate*, decomp. at 143°. When treated in light petroleum with chloroacetyl chloride and aluminium chloride, the methoxyquinoline is slowly converted into *chloroacetyl-8-methoxyquinoline*, a volatile, colourless solid, m. p. 58°, b. p. 152°/22 mm., which powerfully attacks the skin and eyes. Although the action of ammonia on this substance caused resinification, a mixture with potassium phthalimide in a sealed tube at 160—170° gave rise to *phthaliminoacetyl-8-methoxyquinoline*, a colourless solid, m. p. 219°, which by hydrolysis with concentrated hydrochloric acid in a sealed tube was converted into *aminoacetyl-8-methoxyquinoline hydrochloride*, $OMe{\cdot}C_9H_5N{\cdot}CO{\cdot}CH_2{\cdot}NH_2,1\frac{1}{2}HCl$, m. p. 198° (decomp.). D. F. T.

Reactivity of the Methyl Group in 3-Amino-2-methylquinoline. OTTO STARK and FELIX HOFFMANN (*Ber.*, 1913, 46, 2697—2703).—Unsuccessful attempts have been made to involve the methyl group of 2-methyl-3-aminoquinoline in condensations with formaldehyde or carbonyl chloride. Further, ring formation is not observed when 3-amino-2-methylquinoline is diazotised, nor could it be brought about by the elimination of water from 3-acetylamino-2-methylquinoline, although, in the latter case, the basicity of the amino-group is weakened by introduction of the acetyl radicle.

When a solution of 3-amino-2-methylquinoline in hydrochloric acid is warmed with formaldehyde, a salt separates from which



sodium hydroxide liberates the *base* (annexed formula), m. p. 204—205°. The *hydrochloride*, yellow, prismatic needles, m. p. 210—211°, and the *platinichloride*, yellow needles, m. p. 234—235°, were analysed. Boiling aqueous hydrochloric acid slowly decomposes the base into aminoquinaldine and formaldehyde.

Di-2-methylquinolinecarbamide, $C_{21}H_{18}ON_4$, m. p. 278°, is obtained when a solution of 3-amino-2-methylquinoline in dry toluene is left in contact with a solution of carbonyl chloride in the same solvent during two days and the product decomposed with 2*N*-sodium hydroxide. The *hydrochloride*, $C_{21}H_{18}ON_4,2HCl$, pale yellow needles, has m. p. 232—233°.

When a diazotised solution of 3-amino-2-methylquinoline is neutralised with sodium hydrogen carbonate and the precipitate dissolved in ether, a red, crystalline *powder* is obtained (after removal of the solvent), which has m. p. 105—115°, from which a definite substance could not be isolated. A solution of aniline hydrochloride, however, yields *2-methylquinolinediazoaminobenzene*, yellow crystals, m. p. 158°, when added to a diazotised solution of 3-amino-2-methylquinoline hydrochloride in the presence of sodium acetate. The corresponding *aminoazo*-compound, reddish-yellow crystals, m. p. 98—99°, is readily obtained by the usual methods. H. W.

Constitution of the Blood and Bile Pigments. II. HANS FISCHER and ERICH BARTHOLOMÄUS (*Zeitsch. physiol. Chem.*, 1913, 87, 255—269. Compare this vol., i, 209).—Further examples of the coupling of pyrrole nuclei in the 2-position to a carbon atom are described.

Equimolecular quantities of ethyl 2 : 5-dimethylpyrrole-3-carboxylate and ethyl 2 : 4-dimethylpyrrole-3-carboxylate couple with formaldehyde to form *ethyl* 2 : 5 : 2′ : 4′-*tetramethyldipyrrylmethane*-3′ : 4-*dicarboxylate*, $\begin{array}{l}CMe{:}C(CO_2Et)\\ NH\text{———}CMe\end{array}\!\!>C\cdot CH_2\cdot C\!<\!\begin{array}{l}NH-CMe\\ CMe\cdot C\cdot CO_2Et\end{array}$. This forms faintly yellow crystals, m. p. 178—179°. From acetone, it crystallises in long, colourless needles.

Ethyl 2 : 5′ : 2′ : 5-*tetramethyldipyrrylmethane*-3 : 3′-*dicarboxylate*, formed in a similar manner, separates as a colourless, crystalline powder, m. p. 231—232°, after previously sintering.

Ethyl 5-*acetyl*-2 : 4 : 2′ : 4′-*tetramethyldipyrrylmethane*-3′-*carboxylate* crystallises in colourless needles in fan-like aggregates, m. p. 188—189°.

Ethyl 3-*acetyl*-2 : 4 : 2′ : 4′-*tetramethyldipyrrylmethane*-3′-*carboxylate*, crystallises in yellow prisms belonging to the rhombic system, m. p. 231—232°.

Ethyl 3 : 3′-*diacetyl*-2 : 4 : 2′ : 4′-*tetramethyl*-αα-*dipyrrylethane*,

$$CHMe\left(C\!<\!\begin{array}{l}CMe\cdot C\cdot COMe\\ NH-CMe\end{array}\right)_2,$$

obtained on condensing acetyldimethylpyrrole with acetaldehyde, crystallises in colourless, rectangular platelets, m. p. 251—252°.

Ethyl 2 : 4 : 2′ : 4′-*tetramethyl*-αα-*dipyrrylethane*-3 : 3′-*dicarboxylate* separates in well formed, colourless crystals, m. p. 171—172°.

Ethyl 3-*acetyl* 2 : 4 : 2′ : 4′-*tetramethyl*-αα-*dipyrrylethane*-3′-*carboxylate*, crystallises in hexagonal tablets, m. p. 202—203°, but giving a clear flux only at 209°.

5 : 5′-*Diacetyl*-2 : 4 : 2′ : 4′-*tetramethyl*-αα-*dipyrrylpropylene*,

$$CH_2{:}CH\cdot CH\left(C\!<\!\begin{array}{l}CMe{:}CAc\\ CMe\cdot NH\end{array}\right)_2,$$

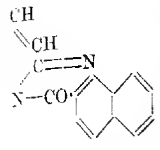
formed on condensing acetyldimethylpyrrole with an alcoholic solution of acraldehyde, was obtained as a yellow, microcrystalline powder.

5-*Bromo*-3-*acetyl*-2 : 4-*dimethylpyrrole*, $NH\!<\!\begin{array}{l}CMe{:}CAc\\ CBr{:}CMe\end{array}$, obtained on brominating acetyldimethylpyrrole in acetic acid, crystallises in faintly yellow prisms, m. p. 165—166° (decomp.).

Pyrroles couple with diazo-compounds more easily in the 2- than in the 3-position. Accordingly, in a mixture of 2 : 4-dimethylpyrrole and 2 : 4-dimethyl-5-ethylpyrrole on the cautious addition of diazobenzenesulphonic acid the former is completely precipitated. On adding more of the diazo-compound to the filtrate, the latter (3-position free) is also completely precipitated as azo-dye. E. F. A.

New Class of Quinoline Dyes. III. EMIL BESTHORN (*Ber.*, 1913, 46, 2762—2770).—The dye, $C_{19}H_{12}ON_2$, obtained by the methods

previously described (Besthorn and Ibele, A., 1904, i, 527; 1905, i, 612), probably has the annexed constitution; it is certainly not 2 : 2′-diquinolyl ketone (Gebhard, A., 1909, ii, 284), since its properties are quite different from those of 2-quinolyl phenyl ketone (A., 1908, i, 681).



The asymmetric structure of the dye is proved as follows. If the dye is 2 : 2′-diquinolyl ketone, it is evident that the substances produced from quinaldinyl chloride and 4-phenylquinoline and from 4-phenylquinaldinyl chloride and quinoline must in each case be 4-phenyl-2 : 2′-diquinolyl ketone. Actually, the two products are different. 4-*Phenylquinaldinyl chloride*, m. p. 116°, and quinoline in benzene at the ordinary temperature yield a *substance*, $C_{25}H_{16}ON_2$, m. p. above 240°, brownish-red crystals, which is converted into carbostyril and 4-phenylquinaldinic acid by concentrated sulphuric acid at 70—75°. The *substance*, $C_{25}H_{16}ON_2$, produced from quinaldinyl chloride and 4-phenylquinoline has m. p. above 240°, forms brownish-red crystals, and yields quinaldinic acid and 4-phenylcarbostyril by treatment with concentrated sulphuric acid at 70°.

In a similar manner, quinaldinyl chloride and ethyl cinchoninate in benzene yield a *substance*, $\begin{array}{l} C_6H_4—N{=\!=}C—CH \\ CH{:}CH·C·CO·N·C_6H_4 \end{array}\!\!>\!C·CO_2Et$, m. p. 238°, brownish-red needles with a green reflex, which resembles other dyes of the same type in forming strongly fluorescent solutions.

These quinoline dyes are more sensitive to sunlight than any other class of organic dyes; a change, however, only occurs in the presence of oxygen. Under such conditions in benzene, the preceding dye is rapidly decolorised, ethyl 2-hydroxycinchoninate being formed, whilst the dye from quinaldinyl chloride and 4-phenylquinoline yields 4-phenylcarbostyril; products corresponding with the other halves of the two molecules cannot be isolated. C. S.

Hydantoins. XXV. The Preparation of Hydantoin from Hippuric Acid. TREAT B. JOHNSON and ROBERT BENGIS (*J. Amer. Chem. Soc.*, 1913, **35**, 1605—1606).—When a specimen of hydantoin is required urgently and potassium cyanate is not available, the following method is convenient.

Hippuric acid (or, indeed, any α-acylamino-acid) is first converted into 3-benzoyl-2-thiohydantoin, which is possible with excellent yields (Johnson and Nicolet, A., 1912, i, 53). This substance is then desulphurised by digesting with an aqueous solution of chloroacetic acid when hydrolysis concurrently occurs, the products therefore being benzoic acid and hydantoin. D. F. T.

Hydantoins. XXVI. Syntheses of 4-Hydroxy-3-methoxyphenylalanine and 3 : 4-Dimethoxyphenylalanine. TREAT B. JOHNSON and ROBERT BENGIS (*J. Amer. Chem. Soc.*, 1913, **35**, 1606—1617).—Vanillin condenses with hydantoin when heated

together with anhydrous sodium acetate in acetic acid, the product being 4-p-*hydroxy*-m-*methoxybenzylidenehydantoin*,

$$\begin{matrix}NH{-}CO\\ |\\ CO{\cdot}NH\end{matrix}\!\!>C{:}CH{\cdot}C_6H_3(OMe){\cdot}OH,$$

a granular solid, m. p. 264—265°; this was reduced by tin and an alcoholic solution of hydrogen chloride with formation of 4-p-*hydroxy*-m-*methoxybenzylhydantoin*, prisms, m. p. 194—195°.

The condensation product of vanillin with 2-thiohydantoin, obtainable under similar conditions to the above, was 2-*thio*-4-p-*hydroxy*-m-*methoxybenzylidenehydantoin*, yellow needles, m. p. 232—233°, which gives a blood-red solution in concentrated sulphuric acid and a yellow one in aqueous sodium hydroxide solution. When digested with an aqueous solution of chloroacetic acid, it undergoes desulphurisation to the above 4-*p*-hydroxy-*m*-methoxybenzylidenehydantoin, and on reduction in aqueous suspension by sodium amalgam becomes converted into 4-*hydroxy*-3-*methoxybenzylthiohydantoic acid*,

$$OH{\cdot}C_6H_3(OMe){\cdot}CH_2{\cdot}CH(CO_2H){\cdot}NH{\cdot}CS{\cdot}NH_2,$$

yellow prisms from aqueous solution, m. p. 181—182° (decomp.). Reduction of the thiomethoxyhydroxybenzylidenehydantoin by tin or by stannous chloride in each case with an alcoholic solution of hydrogen chloride gave the 4-*p*-hydroxy-*m*-methoxybenzylhydantoin described above. The last-named substance when submitted to the action of boiling barium hydroxide solution for many hours evolves ammonia and 4-*hydroxy*-3-*methoxyphenylalanine*,

$$OH{\cdot}C_6H_3(OMe){\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H,$$

prisms (with $1H_2O$), m. p. 255—256° (decomp.), is simultaneously produced.

Veratraldehyde condenses with 2-thiohydantoin, under the conditions described above, with formation of 2-*thio*-4-mp-*dimethoxybenzylidenehydantoin*, prisms, m. p. 229—230°, which can be reduced in suspension in water by sodium amalgam to 2-*thio*-4-mp-*dimethoxybenzylhydantoin*, crystals with $1H_2O$, m. p. 102—103°. When desulphurised by aqueous chloroacetic acid, this gives rise to 4-mp-*dimethoxybenzylhydantoin*, a viscous syrup, from which 3 : 4-*dimethoxyphenylalanine*, hair-like crystals, m. p. 249—250° (decomp.), can be obtained by digestion with barium hydroxide solution.

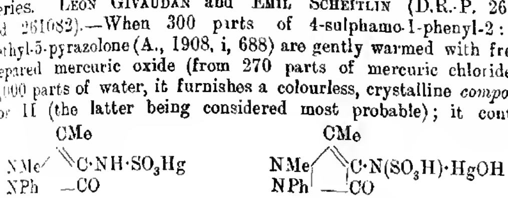
When 4-*p*-hydroxy-*m*-methoxybenzylidenehydantoin is treated with alcoholic potassium hydroxide and methyl iodide, methylation occurs with production of 1-*methyl*-4-mp-*dimethoxybenzylidenehydantoin*, prismatic crystals, m. p. 218°, together with some 1 : 3-*dimethyl*-4-mp-*dimethoxybenzylidenehydantoin*, distorted prisms, m. p. 122—124°, which gives a bright red solution in sulphuric acid. D. F. T.

β-Naphthalaninehydantoic Acid. WILHELM TÜRK (*Biochem. Zeitsch.*, 1913, **55**, 477—480).—Kikkoji (Abstr., 1911, ii, 909) has obtained from the urine, after administration of β-naphthalanine to a dog, a substance to which the formula $C_{15}H_{16}O_3N_2$ was assigned. As it is known that amino-acids on evaporation in urine react with the urea to yield uraminic acids, it is conceivable that the above-mentioned substance is a derivative of this character formed from unchanged β-naphthalanine. By the action of urea on β-naphthalanine in the

presence of barium hydroxide, a β-naphthalaninehydantoic acid, $C_{14}H_{14}O_3N_2$, could be obtained with m. p. 194—195°. Kikkoji's substance melted at 190°, so that the identity of the two products cannot yet be regarded as proved, especially as Kikkoji's analyses are not in strict accordance with those of the synthetic substance.

S. B. S.

Preparation of a Mercury Derivative of the Pyrazolone Series. LEON GIVAUDAN and EMIL SCHEITLIN (D.R.-P. 261081 and 261082).—When 300 parts of 4-sulphamo-1-phenyl-2:3-dimethyl-5-pyrazolone (A., 1908, i, 688) are gently warmed with freshly prepared mercuric oxide (from 270 parts of mercuric chloride) in 10,000 parts of water, it furnishes a colourless, crystalline *compound*, I or II (the latter being considered most probable); it contains



(I.) (II.)

41% of mercury, and, when treated with dilute alkalis, part of the mercury separates in the mercurous condition, leaving a compound in solution containing 24% of mercury.

II. States that by altering the proportions of reacting material in the foregoing preparation, a *compound*, a greenish-white powder containing 67—68% Hg, is obtained, by treatment with sodium hydroxide part of the mercury is eliminated, and the solution furnishes the previously described compound containing 24% of mercury.

F. M. G. M.

Antipyrine and Ammonia Compounds of Some Nitrates of the Rare Earths. ADALBERT KOLB (*Zeitsch. anorg. Chem.*, 1913, **83**, 143—148. Compare A., 1909, i, 16).—*Zirconium nitrate antipyrine*, $Zr(NO_3)_4,6C_{11}H_{12}ON_2$, prepared in nitric acid solution, forms colourless tablets, m. p. 217—218° (decomp.), readily soluble in water. *Thorium nitrate antipyrine*, $2Th(NO_3)_4,5C_{11}H_{12}ON_2$, readily forms supersaturated solutions and has m. p. 168—169°. The *lanthanum*, *cerous*, and *samarium* compounds contain 3 mols. of antipyrine, and have m. p.'s 161—162°, 165°, and 177—178° respectively. *Erbium nitrate antipyrine*, $Er(NO_3)_3,4C_{11}H_{12}ON_2$, forms pink tablets, and has m. p. 175—176°, whilst the *yttrium* compound is colourless and has m. p. 176—177°.

Thorium nitrate combines with ammonia, forming compounds, $Th(NO_3)_4,2H_2O,3NH_3$ and $2Th(NO_3)_4,3H_2O,7NH_3$. An anhydrous salt, formed with the development of much heat, proves to be basic, $ThNO_3(OH)_3$. Zirconium also forms a crystalline basic compound, $ZrO(NO_3)_2,2H_2O,2NH_3$.

C. H. D.

Benzylated Pyrazole Derivatives and a Peculiar Case of Autoalkylation. PAUL JACOBSON and H. JOST (*Annalen*, 1913, **400**, 195—219).—By boiling with about 16% alcoholic potassium hydroxide for one hour, 1-phenyl-2-benzyl-3-methyl-5-pyrazolone decomposes and yields ammonia, 30% of acetoacetanilide, and about 25% of a *substance*,

$C_{24}H_{22}ON_2$, m. p. 152°, colourless leaflets, which proves to be 1-*phenyl-2 : 4-dibenzyl 3-methyl-5-pyrazolone.* The explanation of this curious example of autobenzylation is very probably as follows. The pyrazole nucleus of one molecule of the phenylbenzylmethylpyrazolone is ruptured by the alkali, with the formation of the phenylbenzylhydrazide of acetoacetic acid, $CH_2Ph\cdot NH\cdot NPh\cdot CO\cdot CH:CMe\cdot OH$. Since the union of the benzyl group and the nitrogen atom in benzylated hydrazines is easily loosed, the hydrazide benzylates a second molecule of phenylbenzylmethylpyrazolone forming the substance, m. p. 152°, being itself converted into acetoacetanilide, an atom of nitrogen appearing ultimately as ammonia.

The proofs of the constitution of 1 phenyl-2 : 4-dibenzyl-3-methyl-5-pyrazolone are the following. In accordance with Knorr's experience of 1 : 2-disubstituted pyrazolones, it reacts with alkyl iodides to form ψ-alkyliodides, $CH_2Ph\cdot NI<{NPh\cdot C\cdot OR \atop CMe-C\cdot CH_2Ph}$, which are decomposed by fusion or by aqueous alkalis into the original compound and alkyl iodide. The ψ-*methiodide*, $C_{25}H_{25}ON_2I$, decomp. 234°, pale yellow prisms, prepared at 100°, and the ψ-*ethiodide*, $C_{26}H_{27}ON_2I$, m. p. about 258—260° (decomp.), yellow, crystalline powder, prepared at 120°, are described. The former behaves abnormally with aqueous alcoholic potassium hydroxide in forming, not the original phenyldibenzylmethylpyrazolone, but a *substance*, m. p. 149°, colourless needles (*picrate*, m. p. 176°), the composition of which has not been determined. By heating with 10% sulphuric acid at 130°, 1-phenyl-2 : 4-dibenzyl-3-methyl-5-pyrazolone is decomposed into ammonia, aniline, benzoic acid, and benzylacetone. The authors show that *s*-phenylbenzylhydrazine by similar treatment at 135—140° yields ammonia, aniline, benzaldehyde, and benzoic acid.

In preparing the compound by the benzylation of 1-phenyl-3-methyl-5-pyrazolone, Stolz did not definitely prove the constitution of 1-phenyl-2-benzyl-3-methyl-5-pyrazolone. The authors have now done so, in consequence of the curious behaviour of the substance recorded above. It is converted into benzyl chloride and 5-chloro-1-phenyl-3-methylpyrazole by phosphoryl chloride at 140—150°. By heating in toluene with sodium in an atmosphere of carbon dioxide and subsequent treatment with ice and heating with dilute sulphuric acid, it yields aniline and benzylamine. C. S.

Derivatives of Pyridazine and of Pyrrole. G. KARL ALMSTRÖM (*Annalen*, 1913, **400**, 131—146).—With the exceptions of 4 : 5-diphenylpyridazine and 1 : 3 : 4-triphenylpyrrole, all the unknown diphenylpyridazines and triphenylpyrroles have been prepared.

3 : 5-*Diphenylpyridazin-6-one*, $N<{CPh\cdot CH_2 \atop NH-CO}>CHPh$, m. p. 154—165°, long needles, prepared by warming β-benzoyl-α-phenylpropionic acid and hydrazine hydrate in water, reacts with bromine in boiling glacial acetic acid to form 6-*hydroxy*-3 : 5-*diphenylpyridazine* $C_{16}H_{12}ON_2$, m. p. 183—184°, small needles. The latter is soluble in sodium hydroxide, and is converted by boiling phosphoryl chloride into 6-*chloro-*

3 : 5-*diphenylpyridazine*, m. p. 86—88°, which is reduced to 3 : 5-diphenylpyridazine, m. p. 139—140° (*platinichloride*,

$$2C_{16}H_{12}N_2,H_2PtCl_6,$$

yellow, crystalline powder; *picrate*, m. p. 137—138°), by hydriodic acid, D 1·22, at 160°.

In a similar manner, β-benzoyl-β-phenylpropionic acid and hydrazine hydrate yield 3 : 4-*diphenylpyridazin-6-one*, $C_{16}H_{14}ON_2$, m. p. 217—218°, from which, by methods similar to the preceding, have been successively prepared 6-*hydroxy-3 : 4-diphenylpyridazine*, m. p. 177—178°, 6-*chloro-3 : 4-diphenylpyridazine*, m. p. 110—111°, and 3 : 4-*diphenylpyridazine*, m. p. 106—107° (*platinichloride*, $2C_{16}H_{12}N_2,H_2PtCl_6$, dark yellow, microscopic plates; *picrate*, m. p 155—156°, dark yellow, crystalline powder).

β-Benzoyl-α-phenylpropionic acid and boiling aniline yield 1 : 2 : 4-*triphenylpyrrol-5-one*, $NPh\langle{}^{CPh:CH}_{CO-CHPh}$, m. p. 197—198°, faintly yellow, quadratic prisms. The latter becomes deep green when fused, and almost colourless again after solidification. By treating its solution in acetone and aqueous sodium hydroxide with acetyl chloride at 0°, 5-*acetoxy*-1 : 2 : 4-*triphenylpyrrole*, m. p. 172—173°, almost colourless plates (green when fused), is obtained, whilst phosphorus trichloride at 110—120° converts it into 5-*chloro*-1 : 2 : 4-*triphenylpyrrole*, m. p. 145—146, straw-yellow needles. The latter reacts with phosphoric and phosphoryl chlorides at 140° to form 3 : 5-*dichloro*-1 : 2 : 4-*triphenylpyrrole*, m. p. 152—153°, and is converted by hydriodic acid, D 1·22, and amorphous phosphorus at 150—160° into 1 : 2 : 4-*triphenylpyrrole*, m. p. 151—152°. 5-Chloro-1 : 2 : 4-triphenylpyrrole is converted by hot acetic anhydride and a few drops of concentrated sulphuric acid into 5-*chloro-3-acetyl*-1:2:4-*triphenylpyrrole*, $C_{24}H_{18}ONCl$, m. p. 188—189°, colourless plates, the position of the acetyl group being determined by the fact that the substance is converted into 5-*chloro-3-cinnamoyl*-1 : 2 : 4-*triphenylpyrrole*, $C_{31}H_{22}ONCl$, m. p. 150—151°, by warm alcohol, benzaldehyde, and sodium hydroxide.

β-Benzoyl-β-phenylpropionic acid and boiling aniline readily yield Klingemann's 1 : 2 : 3-triphenylpyrrol-5-one, m. p. 189°, from which 5-*chloro*-1 : 2 : 3-*triphenylpyrrole*, m. p. 165—166°, and 1 : 2 : 3-*triphenylpyrrole*, m. p. 176—177°, have been successively prepared. C. S.

Phenazine. FRIEDRICH KEHRMANN and EM. HAVAS (*Ber.*, 1913, 46, 2820).—Methylphenazonium chloride, bromide, and nitrate can readily be isolated from concentrated aqueous solutions of the methosulphate (compare this vol., i, 298). C. S.

Salts of Azine Dyes. II. FRIEDRICH KEHRMANN, EM. HAVAS, and EUGÈNE GRANDMOUGIN (*Ber.*, 1913, 46, 2802—2808. Compare this vol., i, 908).—The present results are communicated in consequence of the work of Ehrlich and Benda (this vol., i, 904) and of Pummerer and Gassner (*ibid.*, i, 991).

The colour change observed when many azonium bases are converted into salts is not necessarily indicative of constitutive change; in many cases it is due simply to a change in the auxochromic nature of the

amino-group during salt-formation. A number of dyes, such as *apo*safranine, methyl*apo*safranine, 1:3-diaminophenylphenazonium bromide, 3:7- and 3:11-diaminophenylphenazonium chlorides, have been separately dissolved in alcohol and the solutions treated with regulated quantities of concentrated sulphuric acid; the amount of acid required for the production of different colours has been measured. The most important deductions made by the authors are as follows. The number of colours, with a given substance, agrees with the number of basic groups present, indicating that the individual basic groups possess different basicities, and that salt-formation proceeds step by step. Extraordinarily slight basicity is exhibited by all the salt-forming groups in a substance with the exception of one, by which the normal colour is conditioned; all other coloured salts exist only in quite strongly acidic solutions, and are immediately hydrolysed by dilution.

The influence of the position of an amino-group on the colour of the salts is also considered. An amino-group in the meta-position to the azine nitrogen is least influenced by hydrolysis. Its basic character is as strong as that of the amino-group in aniline, and a dye containing such a group forms a diacid salt even with only a slight excess of acid. An amino-group in position 11 (that is, in a phenyl nucleus), whether free or in a salt form, has practically no auxochromic influence. Also, such a group plays no part in strengthening the basicity, 3:11-diaminophenylphenazonium chloride being in this respect similar to *apo*safranine. C. S.

Action of Nitrous Acid on Ethyl Anilino-oximinoacetate. LEOPOLD SEMPER and LEO LICHTENSTADT (*Annalen*, 1913, 400, 302—332).—The substance $C_{10}H_{11}O_4N_3$, m. p. 169°, obtained by Jovitschitsch by the action of nitrous acid on ethyl anilino-oximinoacetate and described by him as ethyl phenyldioxatriazinecarboxylate (A., 1898, i, 93; 1899, i, 239; 1907, i, 98), has the composition $C_{10}H_9O_5N_3$ and m. p. 181·5° when quite pure, and proves to be *ethyl 7-nitro-1:2:4-benzoxadiazine-3-carboxylate*,

$$NO_2\cdot C_6H_3<\begin{matrix}NH\cdot C\cdot CO_2Et\\ O—N\end{matrix}.$$

The yield of the substance is doubled by using 2 mols. of sodium nitrite instead of one (compare Jovitschitsch, *loc. cit.*). It forms a *potassium derivative*, $C_{10}H_8O_5N_3K$, dark red powder, and *benzoyl* derivative, $C_{17}H_{13}O_6N_3$, m. p. 165°, colourless crystals. Although ethyl oxanilate is obtained as a by-product in the formation of ethyl nitrobenzoxadiazinecarboxylate, an intermediate product cannot be isolated; the same substance is also obtained, more slowly, by the action of nitric acid on ethyl anilino-oximinoacetate in glacial acetic acid.

By precipitating ethyl nitrobenzoxadiazinecarboxylate from acetone by water and treating the finely divided suspension with 0·2*N*-sodium hydroxide at 0°, an orange-yellow mass of the extremely unstable *7-nitro-1:2:4-benzoxadiazine-3-carboxylic acid*,

$$NO_2\cdot C_6H_3<\begin{matrix}NH\cdot C\cdot CO_2H\\ O—N\end{matrix},$$

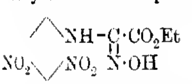
is obtained which can only be examined in the moist state. It decomposes at 118°, yielding nitrobenzoxadiazine, and regenerates the ester by treating its *silver* salt with ethyl iodide. 7-*Nitro*-1:2:4-*benzoxadiazine*, $C_7H_5O_3N_3$, m. p. 240° (Jovitschitsch's phenyldioxatriazine, $C_7H_5O_3N_3$), is obtained from ethyl nitrobenzoxadiazinecarboxylate under the latter's conditions, except that 0·2*N*-sodium hydroxide is employed; the *hydrochloride*, $C_7H_5O_3N_3,HCl$, m. p. above 300°, is a moderately stable, white substance.

By boiling for forty minutes with 0·2*N*-sodium hydroxide (3 mols.), ethyl nitrobenzoxadiazinecarboxylate or nitrobenzoxadiazine is converted into 4-*nitro-2-hydroxyphenylcarbamide*,

$$NO_2\cdot C_6H_3(OH)\cdot NH\cdot CO\cdot NH_2,$$

m. p. 203° (Jovitschitsch's phenyldihydroxydihydrodioxatriazine, $C_7H_7O_4N_3$ [A., 1907, i, 98]), which develops an olive-green coloration with alcoholic ferric chloride, yields 5-nitro-2-aminophenol and 4-nitrocatechol by prolonged boiling with 10% sodium hydroxide, and is converted at 210° into ammonia and nitrobenzoxazolone (nitrocarbonyl-o-aminophenyl), m. p. 241° (St. v. Chelmicky, A., 1891, 52). The preceding transformations suffice to establish the constitution of 4-nitro-2-hydroxyphenylcarbamide. The position of the nitro-group in ethyl 7-nitro-1:2:4-benzoxadiazine-3-carboxylate is proved by the reduction of the ester to 2:5-diaminophenol by boiling alcohol and stannous chloride.

The course of the reaction whereby ethyl anilino-oximinoacetate is converted into ethyl 7-nitro-1:2:4-benzoxadiazine-3-carboxylate by nitrous acid is readily explained in the light of Stoermer's researches on the simultaneous nitriting and oxidising action of nitrous acid on methylaniline and diphenylamine (A., 1899, i, 42). The nitrous acid attacks the aniline group and forms a substance (annexed formula), which, like other such dinitro-compounds, loses nitrous acid with the production of the nitrobenzoxadiazinecarboxylate.



Reactions similar to that exhibited by ethyl anilino-oximinoacetate and nitrous acid are also shown by substances containing the group $NHPh\cdot C(:NOH)\cdot$ attached to $\cdot COPh$ or $\cdot CO\cdot NH_2$. Thus the action of nitrous acid (2 mols.) on anilino-oximinoacetophenone yields 7-*nitro*-3-*benzoyl*-1:2:4-*benzoxadiazine*, $NO_2\cdot C_6H_3{<}\begin{matrix}NH\cdot CBz\\ O{-}{-}N\end{matrix}$, m. p. 178° (decomp.), scarlet needles, which forms a bluish-red solution in alkalis, the solution losing the benzoyl group by long keeping, and yielding 7-nitro-1:2:4-benzoxadiazine. *Anilino-oximinoacetamide*,

$$NHPh\cdot C(:NOH)\cdot CO\cdot NH_2,$$

decomp. 192°, colourless needles, prepared from concentrated aqueous ammonia and ethereal ethyl anilino-oximinoacetate, reacts with nitrous acid (2 mols.) to form chiefly phenyloxamide; a by-product, however, is 7-*nitro*-1:2:4-*benzoxadiazine*-3-*carboxylamide*,

$$NO_2\cdot C_6H_3{<}\begin{matrix}NH\cdot C\cdot CO\cdot NH_2\\ O{-}{-}N\end{matrix},$$

decomp. 240°, yellow crystals, the constitution of which follows from

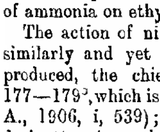
the identity of the substance with the amide produced by the action of ammonia on ethyl 7-nitro-1 : 2 : 4-benzoxadiazine-3-carboxylate.

The action of nitrous acid (2 mols.) on oximinobenzanilide proceeds similarly and yet somewhat differently. Very little benzanilide is produced, the chief product being a *substance*, $C_{13}H_8O_3N_2$, m. p. 177—179°, which is very probably 5-nitro-1-phenylbenzoxazole (Fischer, A., 1906, i, 539); however, a small amount of a benzoxadiazine derivative is probably also formed, because the reaction product develops a deep violet-red coloration with alkalis. C. S.

Preparation of Alkali Soluble Derivatives of Piaselenols [Benz*iso*selenodiazoles]. FELIX HEINEMANN (D.R.-P. 261412).—Benz*iso*selenodiazole, prepared by the action of selenous acid on *o*-phenylenediamine, is insoluble in water and alkalis, and the following compounds have been prepared with a view to eliminate this drawback.

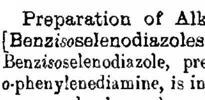
3-*Hydroxybenz*iso*selenodiazole*, $C_6H_4ON_2Se$, yellowish-brown needles, is obtained when an aqueous solution of 3 : 4-diaminophenol hydrochloride is treated with sodium hydrogen selenite (1 mol.); it sinters and reddens at 200°, and has m. p. 209° (decomp.).

*Benz*iso*selenodiazole-3-carboxylic acid*, $C_7H_4O_2N_2Se$, m. p. 222—223°, a crystalline, rose-coloured powder, is prepared in a similar manner from 2 : 3-diaminobenzoic acid.



*Benz*iso*selenodiazole-4-carboxylic acid* is a colourless, crystalline powder with indefinite m. p., darkening at 260°, and decomposing violently at 290°.

When 3-p-*nitro*-o-*sulphobenzeneazotolylene*-2 : 5-*diamine*-4-*sulphonic acid* is reduced it yields 2 : 3 : 5-*triaminotoluene*-4-*sulphonic acid*, and this on treatment with sodium hydrogen selenite gives rise to 4-*amino*-3-*methylbenziso*-*selenodiazole*-6-*sulphonic acid* (formula I); whilst naphthylene-1 : 2-diamine-5 : 7-disulphonic acid (A., 1906, i, 713) furnishes *naphtha*iso*selenodiazole*-5 : 7-*disulphonic acid* (formula II), which is isolated as its crystalline *barium* salt by the addition of barium chloride to the reaction mixture.



F. M. G. M.

Rosinduline Isomerides, Nos. 16 and 17. FRIEDRICH KEHRMANN and MARCELIEN CORDONE (*Ber.*, 1913, **46**, 2974—2979. Compare Abstr., 1899, i, 79).—The condensation of 3-acetylamino-1 : 2-naphthaquinone with phenyl-*o*-phenylenediamine has now been improved and much better yields of the two *iso*rosindulines obtained. The methods of preparation and separation of salts of the two acetyl compounds first formed are described.

10-*Acetylaminophenyl*iso*naphthaphenazonium chloride*,

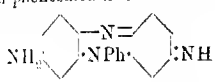
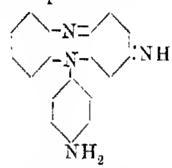
$$C_6H_4<\begin{matrix}N(C_6H_5Cl):C\text{---}C_6H_4\\ N\text{=====}C(NHAc)\end{matrix}>CH,$$

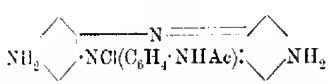
the form in which the substance is isolated, forms crystalline grains.

with a metallic lustre, is almost black, but yields a reddish-brown solution in water, and in alcohol a solution which is olive-green in thin layers and purplish-violet in thick layers. The *platinichloride* forms brownish-black crystals, and the *nitrate*, dark brown needles. The salts dissolve in sulphuric acid to form a violet solution, which, after heating and dilution with water, yields 10-*aminophenyl*iso*naphthaphenazine* (iso*rosinduline*, No. 16); the *nitrate* of this forms small, olive-green needles; the *platinichloride* is an olive-green, crystalline precipitate.

5-*Acetylaminophenyl*iso*naphthazonium nitrate*, the form in which this substance is isolated, is an orange-red, crystalline powder; the *platinichloride* is a brick-red, crystalline precipitate, and the *chloride* crystallises from water in long, brick-red needles on salting-out with sodium chloride. All attempts to eliminate the acetyl group led to further decomposition of the substance. T. A. H.

Constitution of Safranine. Em. Havas and R. Bernhard (*Ber.*, 1913, **46**, 2723—2727).—According to Barbier and Sisley (A., 1908, i, 225), phenosafranine is not a single chemical individual, but consists of a mixture of *indo*safranine (I.) and amino*apo*safranine (II.), commercial phenosafranine containing 85% of the latter compound.

(I.)  (II.) 

(III.) 

A compound of the constitution (II.) has now been prepared by the successive removal of one amino-group and the acetyl group from Ris's *p*-acetylaminosafranine (III.) (A., 1895, i, 148). It possesses the properties of an *apo*safranine, and, therefore, cannot form the main constituent of commercial phenosafranine.

Taken in conjunction with the work of Hewitt, Newman and Winmill (T., 1909, **95**, 577), the present results conclusively prove that phenosafranine is a single chemical individual and has the constitution represented in (I.).

The substances isolated by Barbier and Sisley are either hydrates or homologues, such as occur even in the purest commercial phenosafranine.

Acetylaminosafranine (III) is best prepared by the oxidation of di-*p*-aminodiphenylamine sulphate and acetyl-*p*-phenylenediamine by sodium dichromate in the presence of hydrochloric acid. It may also be obtained by oxidising a mixture of *p*-phenylenediamine, aniline and acetyl-*p*-phenylenediamine. In its appearance, tinctorial properties and absorption spectrum, it very closely resembles phenosafranine.

Aminosafranine is obtained in the form of its *sulphate* by boiling the preceding acetyl derivative with 10% sulphuric acid; the *platinichloride*, $C_{36}H_{32}N_{10}PtCl_6$, was analysed.

When treated with hydrochloric acid and sodium nitrite in alcoholic

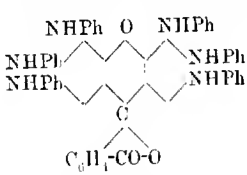
solution, acetylaminosafranine is converted into *aminoaposafranine* (II), which forms a *platinichloride*, $C_{36}H_{30}N_8PtCl_6$, and is very similar to *apo*safranine.

F. B.

The Degradation of Uric Acid by Hydrogen Peroxide and an Iron Salt. KOHSHI OHTA (*Biochem. Zeitsch.*, 1913, **54**, 439—445).—By the treatment of uric acid with a boiling 30% solution of hydrogen peroxide in the presence of a ferric salt until all the uric acid was dissolved, the following products could be isolated. A crystalline substance, $C_3H_6O_3N_4$, which separated on cooling, with m. p. 235°, which is apparently carbonyldicarbamide; a second crystalline substance separated from the mother liquors, which was not obtained pure and could not be identified. In addition, the following oxidation products were found: carbamide, oxalic acid and ammonia.

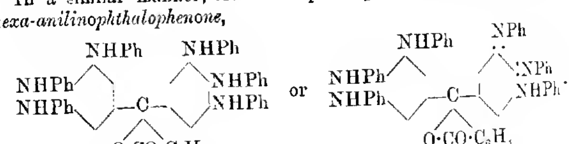
S. B. S.

Action of Aniline on Halogenated Phthaleins. VASSILI V. SCHARVIN (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 885—890).—The fact that anthraquinone derivatives containing hydroxyls, halogens, sodium or sulpho-groups in the α-positions are converted by the action of ammonia or primary amines into aminoanthraquinones which contain amino- or substituted amino-groups and act as stable violet-blue, blue or greenish-blue colouring matters, has led the author to apply this reaction to halogenated phthaleins.



Treatment of eosin with excess of freshly-distilled aniline in a sealed tube at 180—200° yields the *hexaanilinofluoran* (annexed formula), which forms a deep, violet-blue, amorphous powder and yields a bluish-violet alcoholic solution and a pure blue solution in acetic acid. It has no acidic properties, but is faintly basic in character, giving with acids blue salts which exist only in presence of a large excess of acid, and are completely hydrolysed on dilution with water. In dilute alcoholic solution it is readily decolorised by hyposulphite, but gradually resumes its original colour in contact with air.

In a similar manner, tetrabromophenolphthalein and aniline yield *hexa-anilinophthalophenone*,



which is almost identical in colour and properties with the product obtained from eosin. This compound is accompanied by a bromo-derivative containing 4·16% of bromine, which would indicate a more complex molecule than that given above, since one bromine atom remaining in the molecule would correspond with 9·74% of bromine.

An analogous colouring matter was obtained by the action of aniline on chlorinated eosin containing halogen in the third benzene nucleus.

All the above compounds act as substantive colouring matters, and dye silk and wool violet-blue in an acid bath. The absence of the connecting oxygen atom between the two benzene nuclei of the substituted hexa-anilinophthalophenone renders the latter a somewhat less fast colouring matter than the fluoran derivative. These colouring matters may be converted into sulpho-salts soluble in water by treatment at 120° with fuming sulphuric acid containing 12% of sulphur trioxide. T. H. P.

Preparation of Chlorinated Products in the Anthraquinone Series. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D. R.-P. 262076).—Chlorinated products are obtained when diazotised aminoanthraquinones are treated with hypochlorites; the *compound* from anthraquinone-2-diazonium sulphate is a pale yellow powder, decomp. 90°, whilst anthraquinone-2 : 6-bisdiazonium sulphate gives rise to a yellow powder. F. M. G. M.

Saponification of Ethers of Hydroxyazo-compounds. G. CHARRIER and G. PELLEGRINI (*Atti R. Accad. Sci. Torino*, 1913, **48**, 978—981).—These ethers can be readily saponified by acting on them with anhydrous aluminium chloride. When *o*-anisoleazo-β-naphthol is heated for a short time at 120—130° with four or five times its weight of aluminium chloride and the reaction mixture boiled with dilute sodium hydroxide, the *sodium* salt of phenol-2-azo-β-naphthol, $C_{16}H_{11}O_2N_2Na,3H_2O$, is obtained, and from it *phenol-2-azo-β-naphthol*, m. p. 193°, can be prepared. *o*-Phenetoleazo-β-naphthol behaves similarly.

p-Anisoleazo-β-naphthol yields *phenol-4-azo-β-naphthol*,

$$C_{16}H_{12}O_2N_2,$$

which crystallises in cantharides-green needles, m. p. 194°, and the same substance can be prepared similarly from *p*-phenetoleazo-β-naphthol. R. V. S.

***o*-Aminoazobenzene. II.** FELIX II. WITT (*Ber.*, 1913, **46**, 2557—2559. Compare A., 1912, i, 921).—As mentioned in the earlier paper, the researches of Gattermann and Wichmann (A., 1888, 829) indicate that the rearrangement of diazoaminobenzene must give rise to some *o*-aminoazobenzene besides the para-isomeride, because phenylazoiminobenzene, a dehydration product of the former, is present in the reaction product.

By maintaining the temperature below 40° during the rearrangement, the subsequent dehydration is checked, and up to 4% of the ortho-isomeride is found in the product and can be separated by recrystallisation of the mixture from benzene, in which the ortho-compound is much more soluble.

In common with other *o*-aminoazo-compounds (Goldschmidt and Rosell, A., 1890, 616; Goldschmidt and Poltzer, A., 1891, 839; Noelting and Wegelin, A., 1897, i, 155), *o*-aminoazobenzene condenses with aldehydes producing triazine compounds; thus when warmed with

formaldehyde in solution in acetic acid to which a little concentrated hydrochloric acid has been added, it gives 2-*phenyl*-2 : 3-*dihydro*-1 : 2 : 4-*triazine*, $N\langle{-C_6H_4-\atop NPh\cdot CH_2}\rangle N$, yellowish-white needles, m. p. 210° (decomp.); a similar reaction with benzaldehyde in place of formaldehyde gives rise to 2 : 3-*diphenyl*-2 : 3-*dihydro*-1 : 2 : 4-*triazine*, $N\langle{-C_6H_4-\atop NPh\cdot CHPh}\rangle N$, very pale red crystals, decomp. at 215°.

D. F. T.

Hydrolysis of Proteins with an Alcoholic Solution of Hydrogen Chloride. I. CHARLES WEIZMANN and GANESH SAKHARAM AGASHE (*Biochem. J.*, 1913, **7**, 437—440).—The method is an attempt to shorten the usual process, by using a saturated alcoholic solution of hydrogen chloride from the beginning to serve both as a hydrolysing and an esterifying agent. The reagent is not so powerful as an aqueous solution for hydrolysis, as it contains less hydrogen chloride, and cannot be heated to so high a temperature. As expected, therefore, hydrolysis is not so complete. The proteins used, caseinogen and silk fibroin are only partly attacked, and the yield of separate amino-acids is poor.

W. D. H.

Indole Formation in the Hydrolysis of Proteins by Alkalis. E. HERZFELD (*Biochem. Zeitsch.*, 1913, **56**, 82—94).—The indole was quantitatively estimated with the use of the colour reaction with the *p*-dimethylaminobenzaldehyde reagent, the spectrophotometric method of Herzfeld and Bauer being employed. It was found that small amounts of indole are obtainable from proteins on gentle warming with water. If proteins are treated with 0·5% sodium carbonate, indole is also produced; addition of hydrogen peroxide diminishes the amount, but addition of copper sulphate increases it. Similar results were obtained with 0·2% sodium hydroxide solution, but barium and calcium hydroxides gave smaller yields. It was found that larger yields were obtainable by increasing the concentration of the alkali hydroxide, the best results being produced with 9% sodium hydroxide; increase of the alkali concentration beyond this limit diminished the yield. One gram of protein was treated with 1000 c.c. of the alkaline solution. Under optimal conditions, tryptophan itself gives about 60% of the theoretical yield of indole. A pancreatic digestion product of caseinogen yielded 6·5% of the theoretical amount of indole, calculated on the assumption that this protein contains 0·8% tryptophan. Experiments were also arrived at with the object of ascertaining whether pyrrole and scatole are produced at the same time. The colour reactions employed for this purpose are described in some detail. No evidence of the production of these substances could be obtained.

S. B. S.

Separation of Proteins. III. Globulins. HENRY C. HASLAM (*Biochem. J.*, 1913, **7**, 492—516).—The water-insoluble globulin of serum contains, or is closely associated with, rather more than 0·1

phosphorus %. About half of this belongs to a lecithin-like substance which amounts to 8—10% of the globulin freed from ψ-globulin. ψ-Globulin contains no phosphorus. By fractional salt precipitation, the details of which are given, the true globulin, ψ-globulin, and albumin can be satisfactorily separated. W. D. H.

Racemisation of Proteins and their Derivatives Resulting from Tautomeric Change. II. The Racemisation of Casein. HENRY D. DAKIN and HAROLD W. DUDLEY (*J. Biol. Chem.*, 1913, **15**, 263—269).—It has been shown by Dakin (this vol., i, 208) that the treatment of gelatin by dilute alkalis at low temperatures produces racemisation, which is explained on the assumption of a ketol-enol tautomerism of the CH·CO-group. From the character of the amino-acids obtained by hydrolysis, it is claimed that some conception may be formed as to their position in the protein molecule, the occurrence of optically active amino-acids being taken as evidence of their being terminal groups. The preparation of a "racemised" casein is described, which is in fact a hydrolysis product of caseinogen (scission of phosphoric acid having taken place), which on hydrolysis yields inactive alanine, *d*- and inactive valine, *l*- and inactive leucine, *l*-proline and inactive tyrosine, phenylalanine, aspartic and glutamic acids, arginine, lysine, and histidine. As alkalis are used in the synthesis of polypeptides, it is presumed that with present methods it is not possible to synthesise a naturally-occurring protein. S. B. S.

The Proline Fraction Obtained by the Hydrolysis of Caseinogen. The Isolation of Aminobutyric Acid. FREDERICK WILLIAM FOREMAN (*Biochem. Zeitsch.*, 1913, **56**, 1—10).—From the proline fraction of the hydrolysis products, chloroform extracts a non-crystallisable, coloured substance. The residue after extraction with cold alcohol leaves a product which is aminobutyric acid. Further quantities of this substance can also be isolated from the extract in hot alcohol. The cold alcoholic extract when concentrated and treated with cold alcohol yields a precipitate, which is not entirely soluble in amyl alcohol at 60°. From this insoluble fraction, a glassy substance was obtained, which gives a characteristic copper salt, and contains only half its nitrogen in the form of an amino-group, and apparently a piperidine ring. In the same fraction there is also probably a basic substance. There appear to be also in the proline fraction other substances in which the nitrogen is not in the form of amino-groups. A method is also described for preparing fresh *l*-proline, which consists in treating an alcoholic solution of the proline fraction with freshly precipitated, dried and powdered copper hydroxide. The copper salt of the proline passes into solution. S. B. S.

Colloidal Properties of Hæmoglobin. FILIPPO BOTTAZZI (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 141—144).—By dialysis of the colouring matter of blood for four or five months, a pure product is obtained, which is gradually precipitated in the dialyser in very finely-divided form. It consists chiefly of methæmoglobin (95%).

It is almost insoluble in water and in neutral salts, but dissolves on addition of a trace of alkali, yielding a colloidal solution in which the colloid is electronegative. The product also dissolves in presence of a trace of acid, and the colloid in solution is then electropositive.

R. V. S.

The Combinations of Hæmoglobin with Oxygen and Carbon Monoxide. I. ARCHIBALD V. HILL (*Biochem. J.*, 1913, 7, 471—480). —The oxygen and carbon monoxide dissociation curves of hæmoglobin differ according as salts and carbon dioxide are present or not. This has been explained on the theory that the simple molecules of hæmoglobin are aggregated into clusters. This explains all the facts provided two assumptions are made: (1) that the half-saturated molecules Hb_2O_2 and Hb_2CO are unstable, and change into either Hb_2, or $Hb_2(O_2)_2Hb_2(CO)_2$ or $Hb_2{\cdot}CO{\cdot}O_2$; (2) that the half-saturated molecules combine much more readily with carbon monoxide than with oxygen. The first assumption can be explained as due to the fact that Hb_2 is $Hb{:}Hb$, whilst Hb_2O_2 is $:Hb{\cdot}Hb{:}O_2$ with two unsaturated bonds which tend to combine at once with O_2 to form $O_2{:}Hb{\cdot}Hb{:}O_2$. If these assumptions are justified, the deduction may be made that since carbon monoxide combines much more readily with Hb_2O_2 than with Hb, hæmoglobin will take up more carbon monoxide at a given tension if a little oxygen is present than if it is completely absent. W. D. H.

The Combinations of Hæmoglobin with Oxygen and Carbon Monoxide. II. JOSEPH BARCROFT (*Biochem. J.*, 1913, 7, 481—491). —The available data for the dissociation curves of blood agree very closely with the theoretical curves deduced from the following physical conceptions: (1) That the reaction is reversible:

$$Hb_n + nO_2 \rightleftharpoons Hb_nO_{2n};$$

(2) that n is the average number of molecules aggregated together, its value depending on the nature and concentration of the electrolytes in solution; (3) that acids change the equilibrium constant of the reaction without altering the degree of aggregation; (4) that the action does not involve the breakdown and reformation of the aggregates; and (5) that unsaturated oxides are unstable and break up into hæmoglobin and saturated oxides. An entirely similar conception of carboxyhæmoglobin is supported by the available data. So far as the curves deduced from Hill's formula, $\gamma/100 = Kx^n/1 + Kx^n$, can be distinguished from those held by Haldane and Douglas's more complex formula, the experimental evidence favours the former.

W. D. H.

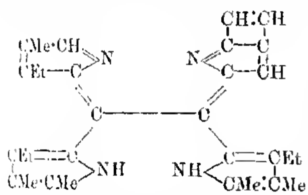
Action of Alkyloxides on Hæmin and its Derivatives. II. Conversion of Hæmin into Mesohæmin. HANS FISCHER and HEINRICH RÖSE (*Zeitsch. physiol. Chem.*, 1913, 88, 9—24. Compare this vol., i, 1006).—By the action either of potassium hydroxide in methyl alcohol or of potassium ethoxide on hæmin, the crystalline iron salt of mesoporphyrin, for which the name mesohæmin is suggested, is obtained. This transformation proves the presence of four pyrrole

nuclei in hæmin. Hæmatoporphyrin likewise yields mesoporphyrin on treatment with alkyloxides, but the quantity is small.

On reducing hæmatoporphyrin solutions with sodium amalgam until they became colourless, crystalline hæmatoporphyrinogen could not be isolated, but the solution of the leuco-base was used for physiological experiments. For two days after injection into rabbits it had no action, on the third day it had a sensibilising action indicating conversion into an active porphyrin. The physiological bearing of the inactivity of the leuco-base is discussed. E. F. A.

Blood Pigments. I. Degradation of Hæmins to the Porphyrins. RICHARD WILLSTÄTTER and MAX FISCHER (*Zeitsch. physiol. Chem.*, 1913, **87**, 423—498).—I. *Constitution of Haemin.*—There is a certain resemblance between the porphyrins derived from hæmin and from chlorophyll; hæmatoporphyrin and mesoporphyrin, for example, having many points of similarity with phyllo-, pyrro-, rodo-, erythro- and rubi-porphyrins. On far reaching degradation of both classes of porphyrins by oxidation or reduction, similar simple pyrrole derivatives are obtained.

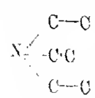
When hæmin and hæmatoporphyrin are heated with potassium hydroxide in methyl alcohol in presence of much pyridine, they are converted cleanly into crystalline porphyrins. Hæmatoporphyrin yields a product *haemoporphyrin* with four oxygen atoms; hæmin gives the complex iron compound of mesoporphyrin. Brief heating of the magnesium derivative of hæmoporphyrin with soda-lime eliminates the carboxyl groups and yields a substance identical with aetioporphyrin, $C_{31}H_{36}N_4$, from chlorophyll in composition, properties, spectrum and basic character. Accordingly, hæmoporphyrin has the composition $C_{33}H_{36}O_4N_4$, which assigns the formula $C_{33}H_{32}O_4N_4FeCl$ to hæmin instead of that usually adopted with 34 atoms of carbon.



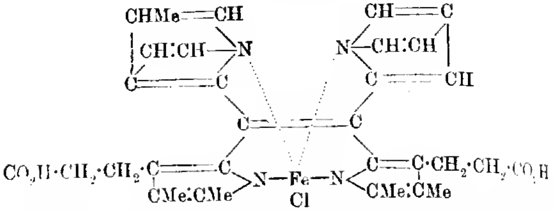
The new formula is in agreement with the analyses of hæmin derivatives and also with the older analyses of Küster (A., 1904, i, 357).

The basic skeleton of aetioporphyrin is composed of four pyrrole nuclei so united that eight hydrogen atoms are spared as compared with simple junction of the nuclei. The formulæ proposed by Küster, Piloty and H. Fischer are replaced by the above representation of aetioporphyrin.

Etiophyllin, $C_{31}H_{34}N_4Mg$, contains magnesium, presumably attached to all four nitrogen atoms. It is assumed that a vinyl residue is united with one of the pyrrole nuclei to a *cyclo*butene ring. The position of this ring and of the substituting methyl groups is uncertain.



It is considered that hæmin contains a bridged ring, such as is known in several alkaloids, in two of the pyrrole nuclei, and it is represented as follows:



When hæmin is converted into hæmatoporphyrin, the two bridged rings are broken, >C:C< becoming ≥C·C≤, and one vinyl residue only becomes coupled with a carbon atom of the pyrrole nucleus. In mesoporphyrin the vinyl group CH:CH is saturated, although analysis does not allow the number of hydrogen atoms in this compound to be settled definitely. This conception is in harmony with the observed unsymmetric way in which the hæmin molecule alters on degradation.

II. *Intermediate products in the formation of haematoporphyrin.*—Aqueous hydrogen bromide saturated at 0° converts hæmin into the *dihydrobromide*, $C_{33}H_{31}O_4N_4FeBr_3$, which crystallises similarly to hæmin in large, obliquely-cut prisms of blackish-blue lustre, and forming a dark blue powder. The solution in concentrated sulphuric acid is a bluish-red.

Hydrogen bromide and acetic acid acting on hæmin yield a *trihydrobromide*, $C_{33}H_{35}O_4N_4FeBr_4$. This forms a brownish-red powder.

When ether is added directly the hæmin has dissolved in the hydrogen bromide-acetic acid mixture; the *salt*, $C_{33}H_{36}O_4N_4Br_2,2HBr$, is obtained in bright red flakes: it is hygroscopic.

When sodium acetate is added to the solution in acetic acid and ether the colour changes from green to brownish-red, and finally the *monoacetate*, $C_{33}H_{36}O_4N_4Br\cdot OAc$, is obtained as a brownish-red powder.

By the action of liquid anhydrous hydrogen bromide on hæmin the iron is eliminated, and a *bromide*, $C_{33}H_{39}O_4N_4Br_5$, obtained in lustrous, violet-red or red, crystalline leaflets.

Liquid hydrogen chloride allowed to act on hæmin for a few minutes only gives rise to a *compound*, $C_{33}H_{36}O_4N_4FeCl_5$, which forms a hygroscopic, lustrous, violet residue. Methyl alcohol converts it into a *dimethyl* ester, crystallising in lustrous, brown, rhombic platelets; it is less basic than any known methyl derivative of hæmatoporphyrin.

By the action of methyl alcohol on the pentabromide a *dimethyl ether dimethyl ester* was obtained, which crystallised in large, lustrous, double pyramids, m. p. 163°.

Hæmin dissolves in liquid hydrogen chloride in sealed tubes with a bluish-red coloration. The product could not be properly purified. Methyl alcohol converted it into a *tetramethyl* compound differing from that above. It crystallises in long, thin, brown, matted needles, m. p. 165°.

III. *Porphyrins with more than four oxygen atoms.*—A convenient method of obtaining hæmin from centrifugalised blood is described.

Hæmatoporphyrin, $C_{33}H_{38}O_6N_4$, previously only known in an amorphous condition, crystallises in lustrous, violet ounded plates, which are reddish-brown by transmitted light. The hydrochloride crystallises in needles which are olive-green under the microscope, but form a red powder. A *dimethyl* ester forms a lustrous, dark red, crystalline crust, m. p. 149°. A second *ester* formed on heating with weaker acid is an intense red powder, m. p. 121°.

The crystalline tetramethyl derivative (Küster and Deihle, this vol., i, 1001) has the molecular weight about 600, agreeing with the formula $C_{33}H_{42}O_6H_4$.

The *dimethyl ether*, $C_{31}H_{34}N_4(OMe)_2(CO_2H)_2$, crystallises in very fine, brownish-red, lustrous, prismatic plates, obliquely-cut and often forming twins resembling a swallow's tail. It sinters on heating, m. p. above 270°.

The *monoacetate*, $OAc{\cdot}C_{31}H_{34}N_4(OH)(CO_2H)_2$, is a bluish-violet powder.

By the action of liquid hydrogen chloride on hæmin and hydrolysis of the intermediate product, $C_{33}H_{37}O_4N_4Cl_6$, with acids, *haeminoporphyrin* is formed, having the composition $(C_{33}H_{37}O_{5.5}N_4)_2$. When heated in a vacuum at 105° no water is eliminated as is the case with hæmatoporphyrin. It forms a heavy, dark violet powder consisting of metallic, rectangular platelets with rounded corners. The *trihydrochloride* forms bright red needles. The *methyl* ester is an intense red powder. Solution in saturated hydrogen bromide and dilution with water converts hæminoporphyrin into hæmatoporphyrin.

Another compound, *haemidoporphyrin*, is obtained from hæmin hydrochloride on treatment with sodium acetate in warm acetone solution. It crystallises in very large prisms with a brownish-violet lustre, and behaves as an hydroxy acid.

All these compounds are differentiated by their basic properties as determined by their distribution between hydrochloric acid and ether (compare Willstätter and Mieg, A., 1907, i, 69).

IV. *Porphyrins with four oxygen atoms.*—Hæmoporphyrin is shown to have the formula $C_{33}H_{36}O_4N_4$. It is more strongly basic than the isomeric porphyrins obtained from chlorophyll. The *dimethyl* ester crystallises in obliquely-cut prisms with a number of twin forms.

On heating hæmin with potassium hydroxide in methyl alcohol and pyridine, the compound, $C_{33}H_{32}O_5N_4FeK_3$, is obtained in long, transparent, red prisms. Mesohæmin is obtained from this in lustrous prisms or thin, yellowish-brown plates. The *dimethyl* ester,

$$C_{33}H_{32}N_4(CO_2Me)_2{:}FeCl,$$

forms brown needles of metallic lustre.

Aetioporphyrin from hæmoporphyrin crystallises in small, reddish-brown prisms with oblique faces, m. p. 265° (decomp.). Despite minor differences, it is shown to be identical with the product derived from chlorophyll. E. F. A.

The Saturated Fatty Acid of Kephalin. JAKOB PARNAS (*Biochem. Zeitsch.*, 1913, **56**, 17—20).—The only fatty acid obtained by the hydrolysis of kephalin with barium hydroxide was stearic acid. There is no evidence of the existence of a "palmitylkephalin"

in addition to the "stearylkephalin" as has been assumed by other authors. S. B. S.

The Nitrogenous Constituent of Kephalin. MONTAGUE H. RENALL (*Biochem. Zeitsch.*, 1913, **55**, 296—300).—An improved process for the preparation of kephalin from ox and sheep brain is described. The disintegrated brain is treated with acetone, then with alcohol, and then with light petroleum. The crude kephalin from the latter extract is precipitated by alcohol, and is purified by precipitating from its solution in ether by alcohol, and from its solution in water by hydrochloric acid. Like the human brain, the brains of ox and sheep contain the nitrogen in the form of a primary base, and in ox brain the presence of aminoethyl alcohol could be detected. S. B. S.

Phosphatides, particularly those in Egg-Yolk. JULIUS EPPLER (*Zeitsch. physiol. Chem.*, 1913, **87**, 233—254).—The products of hydrolysis of that portion of the phosphatides of egg-lecithin which is not precipitated by cadmium chloride consist of aminoethyl alcohol (compare Trier, A., 1912, i, 233) in addition to choline.

The phosphatide soluble in alcohol after complete extraction of egg-yolk with ether is a monaminomonophosphatide.

Comparison of the organic portion of cadmium chloride compounds with the original phosphatides shows a diminution in the amount of carbon, hydrogen and oxygen. Some elimination of fatty acid molecules has perhaps taken place. E. F. A.

Plastein Formation. II. P. GLAGOLEV (*Biochem. Zeitsch.*, 1913, **56**, 195—208).—The grade of formation of more complex products, as measured by the Sörensen formaldehyde titration method, from dialysed hydrolysis products of proteins by dialysed ferments is not smaller than in the case of peptones containing the salt content of ordinary undialysed fermentation mixtures. The addition of salts, however, especially of sodium chloride, facilitates the formation of precipitates during plastein formation. The addition of sodium chloride up to 1·84%, and of calcium chloride up to 0·6% exert no influence on the number of free amino-groups which disappear (as measured by Sörensen's method) during plastein formation; in fact, there is no definite relationship between the amount of precipitate formed during plastein formation and the amount of apparent synthesis, as measured by the diminution of free amino-groups. Plastein formation can also take place in absence of added hydrochloric acid in the presence of dihydrogen potassium phosphate. S. B. S.

Action of Nuclease. P. DE LA BLANCHARDIÈRE (*Zeitsch. physiol. Chem.*, 1913, **87**, 291—309). The gradual liquefaction of sodium α-thymus-nucleate is conveniently followed by viscometric methods. In this way nuclease may be identified, and its activity approximately determined. Nuclease has been proved to be present in the liver, thymus, pancreas, and in the seeds of the soja bean (*Glycina hispida*). The amount is largest in the pancreas. Nuclease is soluble in glycerol. It has a smaller affinity for colloids than trypsin, and may be protected

from tryptic digestion by treatment with colloids or animal charcoal. Yeast-nucleic acid, although differing in composition from thymus-nucleic acid, is hydrolysed by the nuclease of the thymus and the liver. Pancreas extract and the pancreatic secretion behave differently in decomposing nucleic acid. The liquefying and hydrolysing activities of nuclease are not parallel, from which it is inferred that two separate enzymes exist, or that the same enzyme contains two different active groups. E. F. A.

Studies on Amylases. V. Experiments on the Purification of the Amylase of Malt. HENRY C. SHERMAN and M. D. SCHLESINGER (*J. Amer. Chem. Soc.*, 1913, **35**, 1617—1623. Compare A., 1912, i, 815).—By extracting ground malt with two and a-half times its weight of water, dilute alcohol, or very dilute acid phosphate solution at as low a temperature as possible, with subsequent dialysis followed by fractional precipitation by alcohol or acetone, products have been obtained of diastasic power of 1800—2200 (Lintner's scale). The preparations resemble pancreatic amylase in appearance, but are less readily soluble in water; their solutions coagulate at 80°, giving large flocks. D. F. T.

The Action of Maltase on Starch. ZENON WIERCNOWSKI (*Biochem. Zeitsch.*, 1913, **56**, 209—219).—The saccharification of starch by the maltase of maize yields, in every stage, dextrose and soluble starch as the sole products of hydrolysis. The small amounts of dextrins, which yield a violet or red colour with iodine, owe their existence only to the presence of diastase. Maize diastase causes scission of all three kinds of carbonyl bonds in the starch with equal intensity, so that no dextrins are formed as intermediate products. Maize diastase appears, therefore, to be an ideal enzyme for the complete saccharification of starch. S. B. S.

Enzymes. Asymmetric Syntheses through the Action of Hydroxynitrilases. I. VERNON K. KRIEBLE (*J. Amer. Chem. Soc.*, 1913, **35**, 1643—1647).—The result obtained earlier by the author (A., 1912, i, 482) that a certain sample of emulsin when acting on amygdalin gave a residue of *l*-mandelonitrile, whilst its action on a mixture of benzaldehyde and hydrocyanic acid effected the formation of *d*-mandelonitrile can be attributed to the occurrence of varying quantities of two hydroxynitrilases in emulsin, one correlated with the *d*- and the other with the *l*-nitrile.

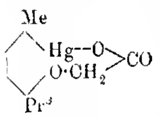
These two enzymes might be expected separately in plants which contain prunasin or amygdalin, and sambunigrin which are glucosides derived from the *d*- and *l*-nitrile respectively. An enzyme activating the combination of benzaldehyde and hydrocyanic acid to *d*-mandelonitrile was actually found in the leaves and bark of *Prunus serotina*, and in the leaves of the peach tree; the product obtained under its influence was not the pure *d*-isomeride, but the small quantity of racemic product present may have been due to the spontaneous combination of the constituents. The amount of racemic product given by emulsin cannot be explained in this way, and is probably to be ascribed to the concurrent action of two enzymes.

The leaf extract of the common elder, which contains sambunigrin, did not give rise to the formation of any optically active compound from benzaldehyde and hydrocyanic acid; whether this is to be explained by the presence of two enzymes concurrently producing *d*- and *l*-isomerides has still to be decided. D. F. T.

The Influence of Acids and Alkalis on the Diastatic Ferment during the Stages of Regeneration. M. J. GRAMENITZKI (*Biochem. Zeitsch.*, 1913, **56**, 78—81).—It has been shown by the author that the properties of the diastatic ferment, which have been lost by heating, can, under certain circumstances, be regenerated on keeping. It is now shown that the regenerative process is inhibited by acid, but accelerated by alkalis in certain low concentrations. This is in direct contrast to the action of acids and alkalis on the extracted ferment, of which the former class of substances function as activators and the latter as inhibitors. S. B. S.

Preparation of Soluble, Stable Derivatives of 3:3′-Diamino-4:4′-dihydroxyarsenobenzene. ANTON DERING (D.R.-P. 261542).—It is found that 3:3′-diamino-4:4′-dihydroxyarsenobenzene hydrochloride combines with albumin acids to furnish compounds which are soluble in water or alkalis, and are of therapeutic value. The preparation of the following *compounds* is described with (1) sodium nucleinate; (2) sodium caseinate; (3) sodium protalbinate; (4) sodium lysalbinate, and (5) from a mixture of sodium protalbinate and lysalbinate; the dry substances are yellow, amorphous masses, the alkali salts greenish-grey lamellæ. F. M. G. M.

Preparation of Nuclear-substituted Mercury Derivatives of Aryloxy-fatty Acids and their Salts. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 261229).—*Mercurithymolacetic anhydride* (annexed formula), a sand-like powder, is obtained when mercuric acetate and thymolacetic acid are heated together in aqueous-alcoholic solution at 70°.



a-Guaiacolpropionic acid, m. p. 55°, is prepared by the action of sodium guaiacol on *a*-bromopropionic acid; on heating with mercuric acetate it gives rise to *mercuri-a-guaiacolpropionic acid*. These compounds are of therapeutic value, and others having the general formula

$$CO_2H{\cdot}R_1O{\cdot}R{\cdot}Hg{\cdot}OH,$$

where R is phenyl, naphthyl or their substituted derivatives, and R_1 alkyl or substituted alkyl groups, are also discussed. F. M. G. M.

Preparation of Soluble Silver Salts of Mercury Derivatives of Hydrocarbons. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO (D.R.-P. 261875).—When the insoluble silver salts of the substituted mercury derivatives of hydrocarbons are treated with the alkali salts of amphoteric or faintly acidic substances they furnish soluble additive

compounds, and the following have been prepared: from hydroxymercurithymoxyl acetate with sodium diethylbarbiturate and from silver hydroxymercuribenzoate with sodium succinimide.

F. M. G. M.

Physiological Chemistry.

Physiological Observations following Descent from Pike's Peak to Colorado Springs. EDWARD C. SCHNEIDER (*Amer J. Physiol.*, 1913, **32**, 295—308).—The return of the blood to a normal state after descent from a great altitude is very slow. Details regarding the percentage of hæmoglobin, red corpuscles, blood volume, pulse rate, alveolar carbon dioxide pressure, etc., are given. The respiratory capacity is not greater in men who live high up than those of similar physique at sea level. W. D. H.

The Respiration of Pulverised Insects. FRED. BATTELLI and (Mlle.) LINA STERN (*Biochem. Zeitsch.*, 1913, **56**, 35—49).—Pulverised insects exhibit a high respiratory exchange, which in certain cases is as large at 40° as that of the living animals, but in others (flies, silk-worm moths) markedly smaller. The respiratory exchange increases with rising temperature up to 30°, and remains from this point constant until about 55°. A slight alkalinity increases in some cases the respiratory exchange, but higher alkalinities exert an inhibitory action, notably on the carbon dioxide production. In acid media both the oxygen consumption and carbon dioxide production are diminished. The gas-exchange takes place both in hypo- and iso-tonic solutions, and is not affected by addition of disodium hydrogen phosphate. It is not much larger in an atmosphere of oxygen than in one of air, and is not influenced by the addition of mammalian blood or of pnein. The addition of trypsin only depresses the respiratory exchange to a small extent. The alcohol and acetone preparations of pulverised insects also exhibit a distinctly high respiratory exchange. Attention is called by the authors to the differences between the respiratory exchanges of pulverised insects and of mammalian tissue; the former are to be ascribed to the presence of oxydases of unknown character.

S. B. S.

The Intensity of the Respiratory Exchanges of Insects. FRED. BATTELLI and LINA STERN (*Biochem. Zeitsch.*, 1913, **56**, 50—58). —The oxygen consumption, carbon dioxide production, and respiratory quotients of cockroaches, silk-worms, and of flies in various stages of development are tabulated. There is an increased respiratory exchange with increasing temperatures. This is also greater in the fully developed insects than in the larvæ, and the latter are more active than the chrysalis. S. B. S.

The Cholesterol and Cholesterol Ester Content of the Blood of Various Animals. FELIX KAUDERS (*Biochem. Zeit.*, 1913, **55**, 96—100).—A series of analytical results obtained by the Windaus digitonin method is tabulated. The cholesterol and cholesterol esters were estimated both in the serum and corpuscles. S. B. S.

Lactic Acid in Blood. WALTER GRIESBACH and SIEGFRIED OPPENHEIMER (*Biochem. Zeitsch.*, 1913, **55**, 323—334).—The formation of lactic acid from various substances by the action of blood corpuscles was investigated. Dextrose, lævulose, mannose, and galactose were found to be capable of forming this acid, whereas arabinose and glucoheptose were not. Inositol was in the majority of cases found to be inactive, but in two cases a slight increase of lactic acid was found. Alanine was indifferent, and glycerol was also generally indifferent, although in one case it gave rise to a considerable amount of acid. It appears as if the same tissue from different individuals of the same species shows an inconstant behaviour as regards the formation of lactic acid from the same substance. S. B. S.

Method for Extraction of Amino-acids from Different Constituents of the Blood. A. COSTANTINO (*Biochem. Zeitsch.*, 1913, **55**, 419—424).—One hundred c.c. of the blood or serum are mixed with 500 c.c. of 2% mercuric chloride solution containing 0·8% hydrochloric acid. The proteins are thereby precipitated. An aliquot part of the filtrate, obtained after centrifugalisation, is evaporated in vacuum after addition of magnesium oxide (in order to separate ammonia) to a small bulk, in which the formaldehyde titration process is carried out. This is done after addition of solid barium chloride and hydroxide, filtering off the precipitate, and neutralising the filtrate to azolitmin. Where very small amounts of amino-acids are present, a certain known amount is added before these manipulations, so that larger amounts of alkali are required for titration. S. B. S.

The Normal Sugar Content of the Blood of Rabbits and Dogs. ADOLF LOEWY and SIEGFRIED ROSENBERG (*Biochem. Zeitsch.*, 1913, **56**, 114—116).—The statement has often been made that the sugar in the blood of rabbits occurs abnormally as a result of the treatment of the animals (binding, exposing the arteries, etc.). The authors now show that a similar phenomenon can be observed in dogs. It was noticed, furthermore, that the blood removed under conditions of local anæsthesia (novocaine) contained less sugar than that removed from the same animals without anæsthetics, and that pain probably has some influence on the abnormally high sugar content in the blood of animals. S. B. S.

Blood Glycolysis: its Extent and Significance in Carbohydrate Metabolism. The Supposed Existence of "Sucre virtuel" in Freshly Drawn Blood. JOHN J. R. MACLEOD [with A. M. WEDD] (*J. Biol. Chem.*, 1913, **15**, 497—514).—Unclotted

(citrate) and defibrinated blood have the same glycolytic power, but potassium oxalate has a depressing action. The rate of glycolysis varies greatly, but in the mean about half the sugar disappears in two and a-half hours at 40°. This is a function of the corpuscles. If much dextrose is added to the blood, the process may be depressed. The rate is the same in diabetic blood. The destruction of sugar in the blood in the intact animal is an almost negligible fraction of the total glycolysis. W. D. H.

Permeability of Blood Corpuscles for Amino-acids. A. Costantino (*Biochem. Zeitsch.*, 1913, **55**, 411—418).—By suspending blood corpuscles in serum in which an excess of amino-acid had been dissolved, and estimating the nitrogenous substances titratable in the presence of formalin, it was found that these diminished in the serum and increased in the corpuscles. From this it follows that the latter are permeable to amino-acids, but, as experiment showed, only up to a certain limit. This corresponded nearly with the amount of amino-acids in the corpuscles of a dog at the time of digestion of food, that is, 45 mg. nitrogen per litre of corpuscles. The amount reached did not differ greatly whether asparagine, the acid hydrolysis products of caseinogen, or glycine was added to the serum. S. B. S.

The Amino-acid Nitrogen, which can be Estimated by the Formalin Method, in the Blood Corpuscles and Serum of Fasting and Fed Animals. A. Costantino (*Biochem. Zeitsch.*, 1913, **55**, 402—417).—The author, by various methods described in some detail, is able to confirm the presence of amino-acids in the blood. The amount in fasting animals is less than that in fed animals, although there is no difference in the amounts in the serum in animals at different stages of nutrition. From this it follows that the excess of amino-acids in the blood of fed animals over that in blood of fasting animals is present in the corpuscles, which must consequently be permeable to these acids. The content of both serum and corpuscles in amino-acids is the same in all parts of the circulation, and this fact negatives the supposition of the deaminisation of the digestion products in the intestinal wall. Lymph contains only a small amount of nitrogen titratable in the presence of formalin. S. B. S.

The Influence of Lipoids on the Coagulation of Blood. Friedrich Rumpf (*Biochem. Zeitsch.*, 1913, **55**, 101—115).—Lipoid emulsions (prepared from ox-brain) hasten the coagulation of oxalate plasma, but only to a slight extent, which is quantitatively far below the action of tissue extracts. There is no species specificity in this action. Plasma which has been deprived of its lipoids by light petroleum will only coagulate after addition of lipoids. This fact does not prove, however, that thrombokinase is a lipoid. The statement of Bordet and Delange, that lipoids, like tissue juices, cause the development of large quantities of thrombin in serum, appears to be incorrect, as the acceleration of clotting

caused by the former is insignificant compared with that caused by the latter (30 : 600). Peptone and hirudin bloods can be made to clot by tissue extracts, but not by lipoids. The lipoids, therefore, do not appear to be the actual active agents, although they do play some part in the clotting process. It seems therefore advisable to retain the term thrombokinase for the active substance of tissue juices. S. B. S.

The Nature of Thrombin and Anti-thrombin. BERTRAM J. COLLINGWOOD and M. T. MACMAHON (*J. Physiol.*, 1913, **47**, 44—53). —Thrombin is destroyed by heat (50—60°), by acid, alkali, and trypsin. After destruction of Gamgee's thrombin, thrombokinase is still present; this preparation also contains fibrinogen. Antithrombin is destroyed by heat (60—65°) and by acid. It will act only in an alkaline medium; neutralisation inhibits, but does not destroy it. The rate of action of antithrombin varies directly with temperature in contrast with thrombin. It is suggested that thrombin is a protein, that antithrombin is a proteolytic enzyme, and that fibrin is a combination of thrombin and fibrinogen. W. D. H.

The Properties of Rabbit's Serum after Treatment of the Animals with Emulsin. KOHSHI OHTA (*Biochem. Zeitsch.*, 1913, **54**, 430—438).—When rabbits have been immunised by several injections of emulsin, their serum exerts a greater inhibitory action on the action of the ferment than the serum of normal animals. This difference of action is, however, only marked when the serum is present in sufficient quantities. If *d*-galactose and dextrose are incubated together in the presence of immune serum, there is evidence of the formation of a disaccharide, of which small quantities of a phenylosazone could be isolated. S. B. S.

Hæmolytic Action of Cyclamin-Cholesterol Mixtures. ERNST H. RIESENFELD and H. LUMMERZHEIM (*Zeitsch. physiol. Chem.*, 1913, **87**, 270—290).—On mixing equivalent quantities of cyclamin and cholesterol, a mixture is obtained in which the hæmolytic action of cyclamin is only partly suspended. Further addition of cholesterol has the effect of lessening the poisonous action. It is therefore inferred that the cyclamin-cholesterol complex is dissociated in solution. If the hæmolytic action of any cyclamin-cholesterol mixture is regarded as a measure of the amount of free cyclamin, it is possible to determine the dissociation constant K of the cyclamin-cholesteride, provided that the total amount of cyclamin and cholesterol in the mixture is known. Constant values for K are obtained by this method so long as the same blood solution is used, but different values of K are obtained with different blood solutions, owing probably to the presence of the serum. The serum has the property of lowering the hæmolytic activity of cyclamin, but acts quantitatively in a very variable manner. E. F. A.

The Hæmolytic Lipoids of the Organs and the Influence on them of Administration of Dextrose. ARNO KIRSCHE (*Biochem. Zeitsch.*, 1913, **55**, 169—188).—Various investigators have shown that the liver contains hæmolytic lipoids, which appear to have a special pathological significance in certain diseases, such as pernicious anæmia. The conception is now advanced that in fatty degeneration of the liver the lipoids are of two-fold origin, namely, those due to degeneration of the cell material itself, and those due to infiltration. To the former class only is to be ascribed the hæmolytic activity. This hypothesis has been tested in the following way: In a number of rabbits fatty degeneration was produced by the following methods: starvation, phloridzin, acute and chronic poisoning with tolylenediamine, maintenance of the animal at high temperatures, post-mortal autolysis. The lipoids were obtained from the liver by heating this organ with alcohol, then extracting with ether, and precipitating the lecithins from the ethereal extract by acetone; after distillation of the ether–acetone mixture the residue was weighed and used for experiment in methyl-alcoholic solution. The hæmolytic value of this solution was then determined. It was found that in all cases, both the quantity of extract and its hæmolytic value were increased in cases of fatty degeneration, especially in that produced by autolysis. Now it is supposed that administration of dextrose inhibits infiltration. A series of experiments similar to the above was carried out with this addition. If the action of sugar is correctly interpreted, then the lipoids derived from the sugar-fed animals should contain relatively larger amounts of fats derived from the cell degeneration, and consequently a higher hæmolytic value. This was actually found to be the case. Attention is also called to differences in the fatty-degenerated livers produced by different methods. S. B. S.

Digestion and Absorption under Normal and Pathological Conditions. EFIM S. LONDON (*Zeitsch. physiol. Chem.*, 1913, **87**, 313—370).—This is a series of short papers on various aspects of the subject carried out on fistula dogs by London's methods.

I. *General Remarks.* E. S. LONDON.—Introductory.

II. *Does Absorption Occur in the Stomach?* J. S. TSCHEKUNÓV.—Many previous authors have stated that absorption occurs in the stomach. In the present experiments finely-divided meat alone or mixed with gliadin was given by the mouth, or solution of dextrose or sodium chloride by the gastric fistula. The material which left the stomach contained the same amount of sugar as given, and protein substances entirely leave the stomach with an accession of nitrogen. In no case was there a deficit in the food material introduced. The proteins were not much broken up in the stomach (amide nitrogen = 11—18%).

III. *Absorption Products of Protein.* N. A. DOBROVOLSKAJA.—Two hundred c.c. of a 5% solution of alanine was placed in the intestine. In five minutes excess of amide nitrogen was found in the blood of the jugular vein. During digestion, the amide

nitrogen rises in the portal blood; the rise in the general blood stream is smaller. In no case did the blood give a biuret reaction.

IV. *The Amount of Amide Nitrogen in the Peripheral Blood during Digestion.* A. D. VOLKOV.—In all stages of digestion the jugular blood contains a small excess of amide nitrogen (almost 4 mg. per 100 c.c. of serum).

V. *The Influence of Surgical Changes in the Stomach on Digestion.* S. F. KAPLAN.—The pyloric section of the stomach plays an important rôle in the proper evacuation of the organ. Hydrochloric acid stimulates the fundus, and inhibits the pylorus. Sodium hydrogen carbonate also stimulates the fundus. Partial extirpation of the fundus hastens the emptying of the stomach. Observations on the rate of emptying an "hour glass" stomach are also given.

VI. *Digestion in Intestinal Resections.* P. P. BRJUCHANOV.—Resection of the jejunum makes no difference on the course of excretion of the constituents of the chyme through a fistula, but the rate of output is raised. The complete compensation for the defect does not, however, occur in the upper section of the digestion canal; the ileum takes no special share in the work of compensation; the main share falls on the large intestine. Opium and tannalbin do not lessen, but increase, the discharge through the fistula. Similar details are given in reference to removal of other parts of the bowel.

VII. *The Course of Digestion of Anomalous Constituents of the Gastric Contents.* R. S. KRYM.—Preliminary digestion of the meat powder given does not hasten the emptying of the stomach. Excess of hydrochloric acid inhibits it.

VIII. *Digestion of Peptonised Milk.* Z. O. MITSCHNIK.—In vitro, peptonised milk is more rapidly digested by gastric, but not by pancreatic, juice. In dogs it causes an increase in the flow of bile. In weakly children, and certain pathological conditions, its use is advised. Further work is in progress.

IX. *The Physiological Importance of the Omentum.* M. R. GILLELS.—The experiments confirm the conclusion that the omentum is of importance, but compensation by the mesentery takes place. Further work is in progress.

X. *The Digestive Glands in Normal and Defective Digestion.* P. P. BRJUCHANOV.—The injection of an aqueous solution of Witte's peptone into the jejunum increases the excretion of bile; this is not affected by acidification of the solution with hydrochloric acid, but if the solution is made alkaline by sodium hydrogen carbonate, it stops the bile flow. Neutral or alkaline peptone solution has no effect on the pancreas, but hydrochloric acid excites a flow of pancreatic juice.

XI. *Maximal Reduction of the Alimentary Tract.* With S. F. KAPLAN.—Experiments are recorded which show how greatly the canal may be reduced without serious harm in dogs. Large amounts of the small intestine, and the whole colon were removed, and the dogs were in good condition months afterwards.

W. D. H.

Absorption of Yeast-Nucleic Acid after Extensive Resection of the Small Intestine in Dogs. JUNICHI MAYESIMA (*Zeitsch. physiol. Chem.*, 1913, **87**, 418—422).—Removal of the greater part of the small intestine in dogs has no practical effect on the absorption of yeast-nucleic acid. Whether this is due to the remnants of the intestine, or to the activity of micro-organisms, is uncertain. W. D. H.

The Influence of Chronic Insufficient Nutrition on Metabolism. NATHAN ZUNTZ, S. MORGULIS, and M. DIAKOV (*Biochem. Zeitsch.*, 1913, **55**, 341—354).—A dog was kept over a prolonged period (more than a year) on a diet insufficient for the energy needs of the organism, during which time the weight sank from [illegible] to [illegible]19 kilos. The animal then died of inanition. The caloric value of the food administered (rice and meat) was controlled during the whole time, and repeated measurements of the respiratory exchanges were made; the nitrogen excreted was also repeatedly estimated. It was found that the energy consumption per square metre of surface sank during this period from 931 cal. per 10 kilos. of weight to a minimum of 631 for half that body weight, and rose again towards the end of the life of the animal to [illegible]21 calories for a weight of 4·1 kilos. There was no indication of a gradual accommodation of the energy consumption to the diminished food supply. S. B. S.

Metabolism during Pregnancy and Lactation. LUDWIG DEBES (*Biochem. Zeitsch.*, 1913, **55**, 124—133).—The gaseous metabolism of a tracheotomised dog during pregnancy and lactation was carried out by a method, described in some detail, based on the Regnault-Reiset principle. The results indicate that there is a large increase in the metabolism during the later stages of pregnancy. During lactation, on the other hand, the increase in the metabolism is relatively small. S. B. S.

The Carbohydrate Metabolism of the Isolated Heart–Lung Preparation. S. W. PATTERSON and ERNEST H. STARLING (*J. Physiol.*, 1913, **47**, 137—148).—Starling and Knowlton stated that the diabetic heart is unable to utilise sugar as well as the normal heart. Further more accurate work has shown that this is not the case. The main purport of the present paper is to withdraw the former conclusions, and explain Maclean and Smedley's results, which seemed to confirm it; the glycogen of the heart muscle is a varying and disturbing factor, which may account for certain discrepancies. The view that the primary factor in diabetes is an absence of the power of the tissues to consume sugar is abandoned. W. D. H.

The Rate of Resorption of Proteins and their Degradation Products from the Small Intestine. HERMANN MESSERLI (*Biochem. Zeitsch.*, 1913, **54**, 446—473).—The experiments were

carried out on a dog with a Thiry-Vella fistula. The various products under investigation were introduced into the fistula, and removed after a definite interval by a method described by the author. The amount of resorption of proteins and degradation products was determined by estimations of nitrogen. All experiments were carried out on the same animal. The amounts of genuine proteins taken up in ten minutes may be represented by the following numbers: Serum, 20; gliadin, 16; caseinogen, 1[illegible]; hæmoglobin, 8. The less degraded proteins, such as peptones, are resorbed more rapidly than the products of complete acid hydrolysis. This fact indicates that the proteins are not degraded completely in the small intestines. During a diet poor in proteins the resorbability of various proteins progressively diminished, but increased again when the animal reverted to a protein-rich diet. This phenomenon was observed, however, only in the first experiments. In later experiments the resorption was less during the subsequent period of rich protein diet. This is probably due to the fact that after the various treatments to which the animal had been subjected, the cells of the intestine had lost their physiological functions as regards the resorption of nitrogenous products. Their capacity for taking up sugar remained, however, unimpaired.

S. B. S.

The Pentoses as a Source of Energy in the Animal Organism P. Schirokich (*Biochem. Zeitsch.*, 1913, 55, 370—3[illegible]). —The experiments were carried out with *l*-arabinose prepared from cherry-gum. It was found that the addition of this carbohydrate to a given basal diet caused very little rise in the respiratory quotient, and about half of the amount ingested was excreted unchanged in the urine. When dextrose was given in corresponding quantities, a certain increase in the respiratory quotient could be ascertained. The increased oxygen consumption, which takes place normally after a meal, is slightly diminished by the addition of dextrose to the diet, and largely diminished by arabinose.

S. B. S.

The Biological Significance of Phosphorus for the Growing Organism. I. The Influence of Phosphorus on the Growth of Animals and on the Phosphorus and Nitrogen Metabolism M. Masslov (*Biochem. Zeitsch.*, 1913, 55, 45—62).—The rate of growth of puppies from three different litters on diets rich and poor in phosphorus was investigated. As basal diets a gruel containing rice, albumin and sugar, cow's milk alone, cow's milk in which the caseinogen was replaced by egg-albumin, which was therefore poor in phosphorus content, and mixed diets of meat, milk, and porridge were employed. The animals were found to thrive only on the mixed diet. The animal fed on milk lived longer than the other animals, but even in this case it finally died of inanition. Phosphorus was added in other experiments after a period on the phosphorus-poor basal diets, in the form either of lecithin, glycerophosphate, or inorganic phosphate. The addition of

lecithin caused a temporary improvement of condition, but in this, as in all the other cases in which phosphorus was added, the animals finally succumbed. The rate of growth when the animals were transferred from a normal to a special diet was not affected immediately, but loss of weight occurred only when they had been a certain time on the abnormal diet. The experiments here recorded do not show conclusively whether the normal growth is due to phosphorus in any special form of combination, or to some other factor. S. B. S.

The Biological Significance of Phosphorus for the Growing Organism. II. The Content of Phosphorus and Intracellular Ferments in the Various Organs. M. MASSLOV (*Biochem. Zeitsch.*, 1913, **56**, 174—194).—The author gives the content in inorganic, organic, and phosphatide phosphorus of the organs of the animals fed by the methods described in the former paper (preceding abstract). The chief loss of the organs during a period of phosphorus starvation is in the inorganic phosphorus. The least loss is in the "organic" phosphorus (nucleoproteins, etc.). The lipoid phosphorus is less stable. Heart and brain do not under any conditions suffer loss in phosphorus, whereas the liver, intestines, muscles, bone-marrow, and kidneys lose considerable quantities during phosphorus starvation. When this loss attains certain limits, the animals die. The only phosphorus compound which produced, when added to the phosphorus-poor diet, an increase in the phosphorus-content of the organs, was lecithin. As regards the intracellular ferments, it was found that on a mixed milk and meat diet, there was a general increase in the fermentative energy of the organs, especially of the lipolytic, amylolytic, and diastatic energy. The development of the catalytic and nucleolytic energies was less marked. Under the influence of phosphorus starvation, not only is there no increase of fermentative energy of the organs, but in certain cases there is a distinct diminution. S. B. S.

The Soft Roes of Fish as Foodstuff for Man. JOSEF KÖNIG and J. GROSSFELD (*Biochem. Zeitsch.*, 1913, **54**, 333—350).—The soft roes from herring and carp were submitted to chemical examination by methods described in some detail, and found to contain meat bases (xanthine and creatinine) and free amino-acids in addition to the protamines, which exist combined with nucleic acid. The fatty substances consist to a large extent of lecithin (20·2—20·7%) and cholesterol (11·2—17·9%). S. B. S.

The Hard Roes of Fish as Foodstuff for Man. JOSEF KÖNIG and J. GROSSFELD (*Biochem. Zeitsch.*, 1913, **54**, 351—394).—The eggs of fish contain a relatively small amount of water as compared with hen's egg; they contain also meat bases, amino-acids, together with ichthulin, as chief protein (which is insoluble in water), albumin, and quantities of fat, which vary in the different species. All the roes investigated contain xanthine substances and creatinine. Xanthine and hypoxanthine were isolated, and the presence of the

following amino-acids was proved, viz., taurine, *l*-tyrosine, and glycine. The presence of thymine was also determined. The proteins contain relatively large quantities of sulphur and phosphorus. No protamines could be isolated from the ichthulins. These substances, on hydrolysis with sulphuric acid, yield purine bases, as Hammarsten and Levene and Mandel have already shown. The ichthulins and albumins yield, furthermore, on hydrolysis, tyrosine, leucine, arginine, histidine, and small quantities of lysine. The ichthulin of carp yields also glutamic acid. The fats contain large quantities of lecithin (up to nearly 60%), and not inconsiderable amounts of cholesterol (3·9—14%). The roes which are poorest in fats contain the largest amounts of lecithin. Caviare and other roes contain free acids, which increase in amount on putrefaction. Of the mineral matter, the acid ions are in excess of the basic ions, as the sulphur and phosphorus are in organic combination.

S. B. S.

Chemical Differentiation of the Central Nervous System. III. Chemical Differentiation of the Brain of the Albino Rat during Growth. WALDEMAR KOCH and (Miss) MATHILDE L. KOCH (*J. Biol. Chem.*, 1913, **15**, 423—448).—The principal chemical changes which occur in the rat's brain during growth are: a decrease in water which begins before medullation sets in; a relative fall in protein due to appearance of lipoids. The lipoids which appear with medullation are cerebrosides and sulphatides. The phosphatides increase before medullation, and occur both in cells and sheaths. Organic sulphur compounds diminish relatively with age, whilst the colloidal sulphur rises. The increase of colloidal matter, which is relatively inactive supporting matter, is one factor in the slowing of metabolism which characterises senescence. W. D. H.

The Action of Ions and Lipoids on the Frog's Heart. A. J. CLARK (*J. Physiol.*, 1913, **47**, 66—107).—An excised frog's heart after perfusion for a few hours passes into a hypodynamic state, and is more readily affected by ionic changes in the fluid perfused. It is improved by increase in the calcium relative to sodium and potassium, and not much improved by increase in hydroxyl ions. The hypodynamic state is caused by a loss of power to combine with calcium. The hydrogen ion concentration must be within narrow limits ($10^{-6\cdot7}$ and $10^{-8\cdot5}$), and a buffer must be present to stabilise the concentrations. A slight increase of carbon dioxide, amino-acids, glycogen, and sugars to a less extent benefit the hypodynamic heart. But the best of all are soaps of the high aromatic fatty acids higher than decoic acid; these soaps form insoluble calcium compounds, but other substances which form similar compounds injure the heart. Serum (but not the serum proteins) is beneficial; the same is true for serum lipoids, lecithin, and saponified serum lipoids. The loss of lipoids is the chief cause of the hypodynamic state; and the function of calcium is to cause an alteration in the colloidal state of the lipoids at the cell-surface.

W. D. H.

The Mucin of the Stomach. J. López-Suárez (*Biochem. Zeitsch.*, 1913, **56**, 167—175).—By extraction of mucin from pig's stomach with 2% potassium hydroxide solution, and addition of acetic acid to the extract, a product was obtained which contained purine bases and also lipoids. By repeated solution in alkali and reprecipitation, a substance free from purine bases could be obtained. This contained (after extraction with alcohol and ether), 53·8% carbon, 7·29% hydrogen, 16·30% nitrogen, 1·47% sulphur, and 4·45% phosphorus. Chondroitinsulphuric acid, prepared from the mucin by Kondo's method, contained 43·3% carbon, 5·47% hydrogen, 5·37% nitrogen, and 4·29% sulphur. The former product contains less oxygen and sulphur than a true mucin, and in other respects differs from it widely in chemical composition. The stomach mucin appears to be a mixture of proteins, in which the chondoprotein is largely replaced by a nucleoprotein. S. B. S.

Carbon Dioxide Formation in the Liver. Eduard Freise (*Biochem. Zeitsch.*, 1913, **54**, 474—502).—An apparatus is described for perfusing liver with blood, and for estimating the carbon dioxide formed in the process, for which purpose the blood is treated with a stream of oxygen, and the mixture of gases is then led through a special absorption apparatus containing barium hydroxide solution. By the artificial perfusion of livers of rabbits or dogs with the blood of calf or ox, 54·74—192·48 mg. of carbon dioxide were formed per minute by 1 kilo. of the organ. This amount could be increased up to 50% by the addition of various oxidisable substances, such as dextrose, pyruvic acid, glyceric acid, and lactic acid. The addition to the blood, on the other hand, of galactose, glyoxylic acid, glycollic acid, and acetic acid, exerted no such influence. S. B. S.

The Effect of Water Ingestion on the Fatty Changes of the Liver in Fasting Rabbits. M. R. Smirnow (*Amer. J. Physiol.*, 1913, **32**, 309—314).—Fasting causes in rabbits fatty infiltration of the liver; if water is given, however, this as a rule does not occur. W. D. H.

Formation of Sugar in the Frog's Liver. Ivar Bang (*Biochem. Zeitsch.*, 1913, **56**, 153—157).—A reply to the criticisms of Lesser (this vol., i, 931). S. B. S.

Glyoxalase. III. The Distribution of the Enzyme and its Relation to the Pancreas. Henry D. Dakin and Harold W. Dudley (*J. Biol. Chem.*, 1913, **15**, 463—474).—This enzyme converts α-ketonic aldehydes, such as methyl- and phenyl-glyoxals, into optically active lactic and mandelic acids. It is probably important in carbohydrate metabolism. It is found in all tissues except the pancreas, which tissue contains an anti-glyoxalase, that is very powerful, and thermolabile. The inhibiting action is not limited to glyoxalase derived from the same species. It is present in pancreatic juice, in commercial pancreatic preparations, and in

the dry state lasts indefinitely (eight years in one case). It is destroyed at 85°, and by digestion with weak hydrochloric acid. Weak alkali is less injurious. The inactivation it produces is a function of the time of action. Whether it is an enzyme or not is unsettled. It is not trypsin, lipase, or diastase. The pyloric caeca of the fish (considered to be homologous with the pancreas) contain no anti-glyoxalase. The blood and tissues of diabetic men and dogs contain less glyoxalase than the normal, but this conclusion demands further work. W. D. H.

Influence of Pancreatic and Duodenal Extracts on the Glycosuria and Respiratory Metabolism of Depancreatised Dogs. JOHN R. MURLIN and B. KRAMER (*J. Biol. Chem.*, 1913, **15**, 365—383).—The effect of injecting pancreatic extract by itself and when mixed with duodenal mucosa extract on the dextrose : nitrogen ratio in the urine of a depancreatised dog, was investigated. This ratio was increased in the day following the injection, but a slight fall followed in the hourly elimination shortly after the injection, which was followed by a compensatory increase. In one case, when the mixed extracts were injected, there was for a short interval a complete disappearance of sugar. A similar effect could be produced by making Ringer's solution as alkaline as the extracts, and a marked diminution of sugar output could also be caused temporarily by injection of 2% sodium carbonate solution. The effects of the extracts are to be explained possibly by the alteration of the acidity. It is also possible that pancreatic extracts alter the permeability of the kidneys. The extracts, within the time of maximal glycosuria, produced no effect on the respiratory quotient, and there is therefore no evidence that they increased the combustibility of sugar in the organism. S. B. S.

The Production and Utilisation of Glycogen in Normal and Diabetic Animals. E. W. H. CRUICKSHANK (*J. Physiol.*, 1913, **47**, 1—14).—After extirpation of the pancreas, the liver rapidly and almost completely loses its glycogen, and becomes loaded with fat. Minkowski's statement that feeding diabetic animals on lævulose produces glycogen-storage was not confirmed. The percentage of glycogen in heart muscle varies, but averages 0·5; it is increased by copious carbohydrate food, and lessened by a diet devoid of protein and carbohydrate. During great activity, the heart may use all its stored glycogen in a few hours. In pancreatic diabetes, the cardiac glycogen rises, and may be entirely consumed if great activity of the heart occurs, as, for instance, after adrenaline. After death, both normal and diabetic hearts contain a glycogenolytic enzyme, so that the glycogen rapidly disappears if the heart is kept warm after the incubation has ceased. W. D. H.

Influence of Extirpation of the Pancreas on the Endocellular Activity of the Liver Diastase. I. ERNST J. LESSER (*Biochem. Z-itsch.*, 1913, **55**, 355—356).—The extirpation of the pancreas from frogs causes changes in the organism in many

respects analogous to those produced by diabetes in the human subject. It was shown that whereas the post-mortem diminution of the liver glycogen in frogs with intact pancreas was 4·2% in three and a half hours at 22°, that of the depancreatised animals was 15·5%. The difference is explained, as the result of the author's previous experiments (this vol., i, 1129), by the assumption that the inhibition of the diffusion of the diastase to the glycogen which exists in the intact frogs has been removed. The experiments were carried out by the method already described, care being taken to keep the livers as free from damage as possible after removal from the body.
S. B. S.

The Physiology of the Glands. XIV. The Function of the Spleen as an Organ of Protein Metabolism, and the Compensatory Processes after Splenectomy. LEON ASHER and HANS SOLLBERGER (*Biochem. Zeitsch.*, 1913, **55**, 13—44).—Immediately after the extirpation of the spleen of a normal rabbit on an iron-rich diet, there is an increase in the hæmoglobin content, and the number of red corpuscles in the blood, which may be explained by diminution of hæmolysis in the absence of the spleen and possibly an increased functioning capacity of the bone-marrow. The withdrawal of a small quantity of blood from the splenectomised animal causes a smaller diminution of hæmoglobin and of blood corpuscles than in a normal animal, and in the former case the blood much more rapidly attains its normal, or even hypernormal, condition. This fact indicates increased functional capacity of the bone-marrow when the spleen is absent. A similar difference between the splenectomised and normal animals was observed when larger amounts of blood were withdrawn. A difference was also observed when the organism was deprived of oxygen by the administration of hydrocyanic acid administered subcutaneously in the form of *aqua amygdalarum amarum*. In the splenectomised animal the treatment resulted again in a smaller diminution of hæmoglobin and red corpuscles, and the reversion to the normal condition of the blood was also more rapid. The extirpation of the thyroids had no specific effect on the hæmoglobin formation in splenectomised animals, or on the effect of hydrocyanic acid on either the splenectomised or normal animals. The general conclusion from the experiments seems to be that on iron-rich diet the functions of the bone-marrow are increased in the absence of the spleen.
S. B. S.

The Intra-renal Resorption of Chlorides in Different Conditions of the Kidney. RAPHAEL LÉPINE and RAYMOND BOULUD (*Compt. rend.*, 1913, **157**, 487—490. Compare *ibid.*, 1913, **156**, 1958).—The resorption of chlorides by the kidneys, on exercising a contra-pressure by means of a canula inserted in the urether and connected to a vessel of water, is reduced to an almost negligible quantity if the water is replaced by a solution of quinine sulphate (1 in 250), or by solutions of numerous toxic substances, or by the use of water after previous section of the splanchnic nerve.
W. G.

The Iodine Content of Fish Thyroids. Alexander T. Cameron (*Biochem. J.*, 1913, **7**, 466—470).—Although iodine has been found in many marine animals, no estimations have hitherto been made for the thyroids of fishes; the percentage in the thyroids of the ray and dogfish averages 1·16%. The highest figure previously obtained in mammals is 0·7 in the dog. W. D. H.

The Carbon Dioxide Formation in Surviving Perfused Muscles. Herbert Elias (*Biochem. Zeitsch.*, 1913, **55**, 153—158).—The hinder extremities of dogs were employed, and they were perfused with ox-blood by the apparatus described by Freise (this vol., i, 1267), whose method of estimating the amount of carbon dioxide formed, was employed. At rest, the muscles produce about 7 mg. of carbon dioxide per kilo. per minute, which quantity can be largely increased by tetanisation (up to fifteen times the amount). S. B. S.

Glycolysis by Muscular Tissue. Alfred Gigon and Max Massini (*Biochem. Zeitsch.*, 1913, **55**, 189—194).—This work was undertaken with the object of reinvestigating the statement of Cohnheim, that sugar is destroyed by incubation with muscular tissue, only in presence of pancreatic substances, as this result has not been confirmed by subsequent observers. A method is described for removal from rabbits of muscular tissue under aseptic conditions. This was disintegrated by freezing with solid carbon dioxide in sterile leather bags and breaking up in the frozen state. It was found that muscular tissue alone, in the absence of pancreas or liver powder, was capable of destroying 85% of the added sugar within twenty-four hours. Salts appear to be necessary for the process, and the best results were obtained when the sugar was incubated with the tissue in Ringer's fluid in the presence of small quantities of sodium hydrogen carbonate. The addition of pancreas, liver, or suprarenal tissue did not appear to increase the amount of sugar destruction. S. B. S.

Pigments. A New Method for the Preparation and a Comparison of the Various Hair Pigments. Hugo Fasal (*Biochem. Zeitsch.*, 1913, **55**, 393—401).—The method of preparation consisted in treating the hair or other keratinous material with twenty-five times the weight of cold saturated potassium hydroxide solution. The protein is thereby dissolved, and the pigment separates; it is purified by dissolving in hot 5% potassium hydroxide solution, in which it dissolves; the solution is filtered off from any undissolved inorganic matter when cold, and the pigment is then precipitated by addition of acid. The examination of hair of different colours indicated that the difference in colour is due to the differences in the amount of pigment, and dark hair which has been deprived of its colour by hydrogen peroxide is nearly free from pigment. White hair contains but very small quantities. The ratio of the amount of pigment in the most strongly coloured hair to that in the least coloured was found to be 30 : 1. S. B. S.

Investigations on Cell Proteins by means of Addition of Formalin. HUGO WIENER (*Biochem. Zeitsch.*, 1913, **56**, 122—152).—The cells of organs of different animals contain soluble proteins, which can be divided into two classes. The chief difference between these is that one class is precipitated by formalin, whereas the other is not. The proteins, which are precipitable by formalin, are considered by the author to belong to the tissue proteins. On washing out the organs in situ, the soluble proteins do not go entirely into the saline solution, owing, apparently, to the semipermeability of the cell-walls. They are only extractible when the cells are destroyed, either by grinding to a paste, or better still, by drying to a powder by Wiechowski's method. If, however, formalin (2%) is added to the saline perfusion liquid, the cell walls are injured, and the semipermeability is destroyed. The soluble proteins can then be readily washed out. In this case, only the soluble proteins which are not precipitated by formalin are obtained. By long perfusion with saline, the walls are also slightly injured, and a small amount of soluble proteins will pass out, so that it is difficult to obtain a perfusion liquid protein-free. Formalin can be used to separate three kinds of protein in the cell, namely, the insoluble proteins, the soluble proteins precipitable by formalin, and the soluble proteins not precipitable by formalin. From a comparison of the amounts obtained from the livers of fed and fasting dogs (the latter, for example, contains small quantities of soluble protein not precipitable by formalin), the conclusion is drawn that the three classes represent stages in the conversion of the protein of the food into the protein of the organ; there is, that is to say, no hard and fast line between the fixed and circulating proteins.

S. B. S.

The Distribution of a Keto-reductase in Tissues. L. VON LAGERMARK (*Biochem. Zeitsch.*, 1913, **55**, 458—462).—Friedmann and Maase have shown that the liver contains a ferment capable of reducing acetoacetic acid to *l*-β-hydroxybutyric acid. It is now shown that this ferment exists also in the muscles and in the kidneys, but not in blood, lungs, the pancreas, or the spleen. The organs investigated were removed from fasting dogs. S. B. S.

Changes in the Reaction of Growing Organisms to Narcotics. HORACE M. VERNON (*J. Physiol.*, 1913, **47**, 15—29).—As tadpoles grow, the narcotising concentration of methyl and ethyl alcohol falls, but that of propyl alcohol remains constant, and of higher alcohols increases; the quotients between the narcotising concentration of successive alcohols vary. The effect of ethyl acetate, propionate, butyrate, and valerate does not alter with age; that of three ketones diminished during growth. The fatal concentrations of monohydric alcohols vary greatly with age. These changes are attributed in most part to changes in the composition of cell-lipoids.

W. D. H.

The Function of the Ferments in the Animal Body after Introduction of Killed Tubercle Bacilli. NINA KOTSCHNEW (*Biochem. Zeitsch.*, 1913, **55**, 481—494).—The introduction of killed tubercle bacilli into rabbits and guinea-pigs caused a diminution of the lipoclastic properties of the serum and organs, and an increase in their antitrypsin and nuclease content. The catalase of the serum and organs was diminished in energy in the case of guinea-pigs only. There was a slight diminution of the amylase and diastase content of serum and organs. S. B. S.

The Presence of Adenase in the Human Body. ESMOND R. LONG (*J. Biol. Chem.*, 1913, **15**, 449—462).—Adenase could not be found in human adult liver, the placenta or fœtal liver, brain, bone, thymus, stomach, intestine, pancreas, lungs, and spleen. It is, however, present somewhere in the fœtus, for if the entire fœtal material is mixed with adenine, hypoxanthine is formed. Hypoxanthine is always formed in the autolysis of human tissues, and in the absence of adenase is probably due to the action of adenosine deamidase and inosine hydrolase. W. D. H.

The Tyrosineoxydase, Polyphenoloxydase, and Oxydones of Insects. FRED. BATTELLI and LINA STERN (*Biochem. Zeitsch.*, 1913, **56**, 59—77).—All the above ferments are contained in the insects investigated. The fully developed insect contains less polyphenol oxydase than the larva and chrysalis of the same species. *p*-Phenylenediamine is oxidised less energetically than quinol and pyrogallol by pulverised insects, which is in marked contrast to the action of vertebrate tissue. There is no parallelism between the polyphenoloxydase content of insects and the respiratory exchange of the living insect. As a rule, those insects which have the largest content in polyphenoloxydase have also the largest amount of tyrosineoxydase. Both ferments can be obtained in powder form by treatment of an insect paste with acetone or alcohol. Tyrosine is oxidised with evolution of carbon dioxide. Insects contain no uricoxydase. There is no alcohol oxydase in silk-worms. Insects contain a succino-oxydone, but the oxidation of succinic acid is much weaker than that of the polyphenols and tyrosine. This oxidation is also weaker in the case of insects than in the case of muscular or liver tissue of mammals. There is a rough parallelism between the oxidation of succinic acid by pulverised insects and the oxidation energy of the living animals. Citric acid is not oxidised by insect paste, and the intensity of the oxidation by pulverised insects is uninfluenced by the addition of sodium acetate, sodium lactate, or dextrose. S. B. S.

Physical Properties and Chemical Composition of Frog's Urine. SHOZO TODA and KATSUTA TAGUCHI (*Zeitsch. physiol. Chem.*, 1913, **87**, 371—378).—The reaction of frog's urine is usually feebly acid to litmus paper; D 1·0009 to 1·0018; $\Delta = 0{\cdot}106$. The electrical conductivity in reciprocal ohms is $0{\cdot}78 . 10^{-3}$. In summer frogs the urine contains 0·193 of organic and 0·053 of inorganic con-

stituents %; of the latter 0·0467 are salts soluble in water. There is a relative large amount of phosphoric acid and sodium. The proportion of sodium to potassium is 1·7 : 1. W. D. H.

The Chemistry of Cancerous Tumours. B. WOLTER (*Biochem. Zeitsch.*, 1913, **55**, 260—265).—Analyses of the total phosphorus and its distribution as inorganic, phosphatide and protein phosphorus from a liver sarcoma, from the surrounding liver tissue, and from the tissue of normal liver, are given. The most marked difference in the analyses of the tumour and other tissues was the somewhat smaller percentage (both relative and absolute) of the phosphatide phosphorus in the former. The amount of cholesterol in the tumour was 0·25% of the fresh tissue. S. B. S.

Disturbances in the Protein Metabolism in Cancer. (The Excretion of Thiocyanates.) PAUL SAXL (*Biochem. Zeitsch.*, 1913, **55**, 224—244).—It has been found that the urine in cases of cancer generally contains excess of nitrogen, but the amount of urea is less than the normal, whereas the quantities of oxyproteic acid and ammonia are greater. The urine of cancer patients is also characterised by containing a certain amount of sulphur in a form in which it is readily oxidised to sulphuric acid. These results suggest the presence of thiocyanates, due to hydrogen cyanide, split from proteins, and not completely oxidised. Similar urines were obtained from normal individuals after administration of thiocyanates. It is now directly shown that, in the majority of cancer cases, the urine contains abnormally large amounts of thiocyanate, which is the source of the easily oxidised sulphur. Other pathological urines also yield abnormally large amounts, but not to quite the same extent as those from cancer patients. The thiocyanate was estimated by precipitation with silver nitrate in acid solution; the silver salt was then dissolved in sodium hydrogen carbonate, and treated with excess of $N/10$-iodine solution and potassium iodide. After four hours, hydrochloric acid is added, and the excess of iodine estimated by titration. The amount of thiocyanate can be calculated from the equation:

$$CNSK + 3I_2 + 4H_2O = H_2SO_4 + 5HI + KI + HCN.$$

S. B. S.

Protozoan Protoplasm as an Indicator of Pathological Change. II. In Carcinoma. FRANK P. UNDERHILL and LORANDE LOSS WOODRUFF (*J. Biol. Chem.*, 1913, **15**, 401—414).—Extracts of breast cancer depress the division rate of *Paramæcium*, and kill the protozoon. Extracts of normal mammary tissue do not possess this property. Weak concentrations of the abnormal extracts may stimulate the *Paramæcium*. W. D. H.

The Tryptophan Content of Normal and Pathological Cutaneous Tissues, and of Malignant Tumours. HUGO FASAL (*Biochem. Zeitsch.*, 1913, **55**, 88—95).—By means of the author's colorimetric method, the tryptophan content in various normal

and pathological tissues was estimated. The epidermis is relatively rich in this substance, as are certain tumours, such as carcinoma of the liver. Mammary tumours, on the other hand, do not contain a trace. S. B. S.

A Case of Pentosuria. PHŒBUS A. LEVENE and FREDERICK B. LAFORGE (*J. Biol. Chem.*, 1913, **15**, 481—486).—Neuberg states that the usual pentose in cases of pentosuria is *dl*-arabinose. Elliott and Raper described a case in which it was probably ribose. In the present case much of the pentose was lost in the methods adopted for its separation, and the identification of the sugar was not complete, but it was probably *l*-ribose. W. D. H.

The Origin of the Sugar Secreted in Phloridzin Glycosuria. RAPHAEL LÉPINE and RAYMOND BOULUD (*Compt. rend.*, 1913, 157, 530—532. Compare A., 1904, ii, 753).—The authors quote experiments which, they maintain, contradict the generally accepted hypothesis that the sugar eliminated in phloridzin glycosuria comes from the renal cells. They consider that the point of attack of the phloridzin in the kidney is the vascular endothelium. W. G.

The Production of Fever. MAX CLOETTA and ERNST WASER (*Arch. expt. Path. Pharm.*, 1913, **73**, 436—456).—By subcutaneous and intravenous injection of the monomethyl derivative of alicyclic tetrahydro-β-naphthylamine, the body temperature is raised in a few minutes. This rise occurs in the region of the cerebral ventricles within twenty seconds, and in the fore-brain in about forty to sixty seconds; the intestinal temperature rises next, and finally that of the skin (which falls during the first half minute). If death occurs, the intestine and skin remain warm after the temperature falls in the central nervous system. W. D. H.

Protozoan Protoplasm as an Indicator of Pathological Changes. I. In Nephritis. LORANDE LOSS WOODRUFF and FRANK P. UNDERHILL (*J. Biol. Chem.*, 1913, **15**, 385—400).—Extracts of normal kidneys from well-fed and starving animals exert no effect on the division rate of *Paramœcium*; but extracts of nephritic kidneys depress it. This is not due to accumulation of tartrate which was given to induce nephritis. The experiments were made on rabbits. W. D. H.

The Chemistry of the Leucocytozoon Syphilidis and of the Hirt's Protecting Cells. JAMES E. R. McDONAGH and R. L. MACKENZIE WALLIS (*Biochem. J.*, 1913, **7**, 517—543).—Much of the work recorded relates to the properties of the colloidal dyes used for micro-chemically investigating the syphilis parasite. Basic stains are most suitable for work in vivo, and of these borax-methylene-blue is the best. The parasite has a lecithin-globulin envelope which stands out more clearly by adding dextrose to the stain. The varied affinity shown for methylene-violet and methylene-red is due to the prevalence of a substance which has

strong reducing properties (lecithin-globulin), and not to a change in the reaction. Details are given of the staining reactions of different parts of the parasite, but tho whole subject is at present of subsidiary chemical interest. W. D. H.

(Pharmacological) Action of Bromine Salts. E. BERNOULLI (*Arch. expt. Path. Pharm.*, 1913, **73**, 355—397).—The theory of chlorine poverty is insufficient to explain the action of alkali bromides. For the neutralisation of the bromine action, the administration of chlorides is not necessary, but other salts (sodium sulphate and nitrate) act in the same way. Bromine salts cause changes in the colloidal material of the central nervous system. The bromine ions which take the place of chlorine ions alter the aggregation state of the cell-colloids, probably in the direction of greater swelling, and thus is produced a functional change in the nerve-cells. W. D. H.

The Action of Leucocytes and Other Tissues on *dl*-Alanine. PHŒBUS A. LEVENE and GUSTAV M. MEYER (*J. Biol. Chem.*, 1913, **15**, 475—480).—Leucocytes under aseptic conditions form *d*-lactic acid from hexoses, regardless of the configuration of the hexose. The conversion of amino-acids into hydroxy-acids is analogous to the change of methyl-glyoxal into lactic acid; thus, alanine is transformed into lactic acid through the stage of pyruvic acid. Dakin, Dudley and Ringer found in diabetic dogs fed on pyruvic acid that the yield of sugar was smaller than from either alanine or lactic acid. Hence in the present research the action of leucocytes was tested on various forms of alanine. The unexpected result obtained was that neither leucocytes nor kidney tissue had any effect at all on *dl*-alanine. W. D. H.

The Behaviour of Pyruvic Acid in the Animal Body. II. GUSTAV EMBDEN and MAX OPPENHEIMER (*Biochem. Zeitsch.*, 1913, **55**, 334—340. Compare A., 1912, ii, 1075).—As pyruvic acid is a possible intermediate product in the conversion of alanine into lactic acid, it was of interest to ascertain whether the latter acid could be obtained directly from the former in the animal body. It was found that this change could be accomplished when pyruvic acid was perfused through a glycogen-poor liver of a dog which had been starved for four days. It was obtained in the *d*-form. S. B. S.

The Behaviour of Pyruvic Acid in the Animal Body. III. The Formation of Sugar and Lactic Acid from Pyruvic Acid. PAUL MAYER (*Biochem. Zeitsch.*, 1913, **55**, 1—3).—The author recapitulates his former results, which indicate that pyruvic acid, on administration to rabits and dogs, causes hyperglycæmia and glycosuria, but that on administration to animals treated with phloridzin, it causes a diminution of the sugar and nitrogen output in the urine, owing apparently to a toxic action on the kidneys. He is not able to explain the difference between his results and those obtained by A. J. Ringer and by Dakin and Janney (this vol.,

i, 937), but rejects the explanation offered by the former. Animals to which pyruvic acid has been administered excrete in the urine both *dl*- and *d*-lactic acids. S. B. S.

The Degradation of Carboxylic Acids in the Animal Body. XV. The Behaviour of Benzaldehyde in the Animal Body. ERNST FRIEDMANN and WILHELM TÜRK (*Biochem. Zeitsch.*, 1913, 55, 425—431).—After administration of benzaldehyde to dogs, only hippuric acid and small quantities of benzoic acid, but no cinnamic acid, could be isolated in the urine. The cinnamic acid found by Dakin after administration of phenylpropionic and phenylvaleric acid must be due therefore to degradation, and not to synthesis by condensation of an aldehyde with acetic acid. S. B. S.

The Degradation of Carboxylic Acids in the Animal Body. XVI. Behaviour of α-Phenylbutyric Acid in the Animal Body. ERNST FRIEDMANN and WILHELM TÜRK (*Biochem. Zeitsch.*, 1913, 55, 432—435).—As γ-phenylbutyric acid undergoes in the animal body oxidation in the β-position to yield a keto-acid and finally phenylacetic acid, it was of interest to ascertain how the α-acid $CH_3\cdot CH_2\cdot CHPh\cdot CO_2H$ would behave. If oxidation were to take place in the β-position, phenylacetic and acetic acid should be expected as final products, according to the equations given by the authors. As a matter of fact, only unchanged α-phenylbutyric acid, and a neutral substance, which was not further investigated, could be isolated in the urine of dogs, to which this substance had been administered. S. B. S.

The Degradation of Carboxylic Acids in the Animal Body. XVII. Formation of Acetoacetic Acid from Acetic Acid in the Perfusion through the Liver. ERNST FRIEDMANN (*Biochem. Zeitsch.*, 1913, **55**, 436—442).—Adam Loeb has shown that the addition of sodium acetate to the blood perfused through the surviving liver of a dog causes a marked increase in the amount of acetoacetic acid formed. This is in contrast to the author's own results, where no such increase was found. It is now shown that this increase only results when the liver is poor in glycogen, as, for example, in the livers of animals which have been starved and tetanised by strychnine. In this case increase of acetoacetic acid only follows when acetate is added to the perfusing blood. Such an addition causes no increase when the livers used for experiment are rich in glycogen and taken from a well-fed animal. The mechanism of the formation of acetoacetic acid from acetic acid is discussed, and it is suggested that acetaldehyde is an intermediate product, which condenses with acetic acid to form crotonic acid, from which, by addition of water and oxidation, acetoacetic acid is formed. It is further suggested that in presence of carbohydrates, acetic acid is condensed in some other way. From the fact that acetoacetic acid is only formed from fatty acids with an even number of carbon atoms, the conclusion is drawn that acids do not always form β-keto-acids as intermediary oxidation products.

as in this case acetic acid should always be formed, and this is, as the experiment shows, an acetoacetic acid former. S. B. S.

The Degradation of Carboxylic Acids in the Animal Body. XVIII. Behaviour of Glycollic and Glyoxylic Acids in Perfusion through the Liver. JUNICHI MOCHIZUKI (*Biochem. Zeitsch.*, 1913, **55**, 443—445).—Friedmann has suggested (see preceding communication) that acetoacetic acid is formed from acetic acid in perfusion experiments by condensation of the latter with acetaldehyde to yield crotonic acid as an intermediate product. It follows, if this suggestion is correct, that no acetoacetic acid should be formed if the methyl group of acetic acid should have a hydrogen replaced by hydroxyl. As a matter of fact, it was found that neither from glycollic nor glyoxylic acid is acetoacetic acid formed.
S. B. S.

The Degradation of Carboxylic Acids in the Animal Body. XIX. Acetoacetic Acid Formation in the Perfusion of Livers Rich in Glycogen. JUNICHI MOCHIZUKI (*Biochem. Zeitsch.*, 1913, **55**, 446—449).—It has been shown by Friedmann (this vol., i, 1276) that acetoacetic acid is formed from acetic acid only when perfused through livers poor in glycogen. It is now shown that butyric acid, β-hydroxybutyric acid, crotonic acid, and *iso*valeric acid yield acetoacetic acid when perfused through livers rich in glycogen, whence the conclusion is drawn that acetic acid is not an intermediary product of reaction. S. B. S.

The Degradation of Carboxylic Acids in the Animal Body. XX. Conversion of Crotonic Acid into *l*-β-Hydroxybutyric Acid by Liver Pulp. ERNST FRIEDMANN and C. MAASE (*Biochem. Zeitsch.*, 1913, **55**, 450—457).—Crotonic acid is converted into *l*-β-hydroxybutyric acid in the presence of liver pulp obtained from a fasting dog. Carbon dioxide inhibits the reaction. S. B. S.

The Fixation of the Digitalis Substances in the Animal Organism, Considered more Especially with Reference to their Behaviour in the Blood. ERNST OPPENHEIMER (*Biochem. Zeitsch.*, 1913, **55**, 134—152).—Various investigators have failed to detect these substances in the tissues after injection into animals, and researches were undertaken to ascertain the cause of this failure. It was found that the slightly soluble digitoxin is only slowly precipitated from its alcoholic solution. The solutions of both amorphous, slightly insoluble, digitalis glucosides are dialysable, and behave in this respect like the easily soluble crystalline glucosides, strophanthin and antiarin. As precipitation in the blood-stream does not account for the apparent absence of the substances in the blood-stream, the effect on their toxic action due to the admixture with serum was determined, Straub's method for estimating the toxicity (action on frog's heart) being employed. It was found that serum could diminish or destroy the toxicity of the following substances: digitoxin, gitalin, digitalin, oleandrin,

saponin, and methyl-violet. It increased the toxicity, on the other hand, of strophanthin and antiarin. This action of the serum cannot be replaced by either cholesterol, egg-white, or lecithin in Ringer's fluid. These experiments indicate that the failure to detect digitalis alkaloids after injection into the organism is not due to its fixation by cells of the tissues. S. B. S.

Action of Enzymes on Racemised Proteins and their Fate in the Animal Body. HENRY D. DAKIN and HAROLD W. DUDLEY (*J. Biol. Chem.*, 1913, **15**, 271—276).—"Racemised" casein and caseose are resistant to the action of pepsin, trypsin, and erepsin. On feeding the substances to a dog *per os*, they were excreted unchanged in the fæces, no absorption having taken place in the intestine. It appears as if this organ can take up only comparatively simple substances. Racemised caseose, when administered subcutaneously to a dog, produced no symptoms, and was excreted unchanged in the urine. "Racemised" casein remained unchanged in the presence of bacteria, but the caseose was slowly attacked, yielding indole and other products. S. B. S.

The Behaviour of Iodoprotein in the Organism. JULIUS WOHLGEMUTH and BRUNO REWALD (*Biochem. Zeitsch.*, 1913, **55**, 7—12).—The preparation of an iodine derivative from coagulated blood by means of an alcoholic solution of iodine is described, which contains about 15% of iodine and 0·25% of iron. Preliminary therapeutic experiments indicate that this preparation is well tolerated in relatively large doses by rabbits, dogs, and man. In the experiments on rabbits, it was shown that the iron accumulates in the liver. The preparation is readily absorbed, and about 70% of the iodine is excreted in the urine between the third and forty-eighth hours after administration. Little or no iodine is found in the fæces. S. B. S.

Degradation of the Naphthalene Ring in the Animal Body. ERNST FRIEDMANN and WILHELM TÜRK (*Biochem. Zeitsch.*, 1913, **55**, 463—476).—β-Naphthylalanine and β-naphthylpyruvic acid are degraded in the organism to benzoic acid. In order to study the influence of the side-chains on the degradation of the naphthalene nucleus, the degradation of the following products was studied: β-naphthoic acid, β-naphthylacetic acid, and (in greater detail) β-naphthylpyruvic acid. The former results with the last-named were confirmed, in that in the urine of dogs to which it had been administered an excess of hippuric acid was found. This did not happen in the case of either the naphthoic or naphthylacetic acids. The pyruvic acid derivative, however, yielded hippuric acid only when administered *per os*, but not when subcutaneously applied, and the conversion into benzoic acid is therefore possibly a putrefactive process in the intestines. After administration of β-naphthoic acid, in addition to unchanged product, naphthuric acid was found in the urine both after administration *per os* and after injection under the skin. A conjugation with glycine had

therefore taken place. After administration of β-naphthylacetic acid, a considerable amount of unchanged product was found in the urine. The fate of the remainder is still unknown. S. B. S.

The Influence of the Subsidiary Alkaloids of Opium on the Action of Morphine. RICHARD MEISSNER (*Biochem. Zeitsch.*, 1913, 54, 395—429).—The experiments were carried out with a view to demonstrate the potentialising capacity of other alkaloids on the pharmacological action of morphine, as shown by Straub. The action on the respiratory centre of rabbits, the narcotic action on cats, and the action on the isolated intestine of rabbits were investigated. A larger diminution in the respiratory volume was produced by narcophine, but apart from this, no essential difference was found in the actions of narcophine, pantopone, or laudenone. The investigations appear to negative the conception of a potentialising action of narcotine on morphine. Nevertheless, the results must be accepted with some caution, in view of some quoted experiments of Zehbe on the action of various preparations on the human intestine. S. B. S.

Degradation of Phenylalanine in the Animal Organism. GUSTAV EMBDEN and KARL BALDES (*Biochem. Zeitsch*, 1913, 55 301—322).—The general theory as to the relationship between the combustibility of amino-acids in the normal organism, their convertibility into homogentisic acid in alcaptonuric individuals, and their conversion into acetoacetic acid when perfused through the liver is discussed. Phenylpyruvic acid, a conceivable first oxidation product of phenylalanine, both of which substances are burnt up in the organism and converted into homogentisic acid in alcaptonuric cases, might be expected, like substances generally with this behaviour, to be convertible into acetoacetic acid by perfusion through the liver, especially as phenyl-lactic acid, and the keto-acid corresponding with tyrosine, undergo this change. This was found, however, not to be the case; on the contrary, phenylpyruvic acid even inhibits the acetoacetic acid formation from phenylalanine, tyrosine, leucine, and *p*-hydroxyphenylpyruvic acid when these are perfused in its presence. On the other hand, it does not inhibit acetoacetic acid formation from *iso*valeric or *n*-hexoic acids, and does not therefore act as a general inhibitor of oxidation processes in the liver. It possibly combines with the side-chains in the cell to which the amino-acids are normally attached when converted into acetoacetic acid. These facts suggest that phenylpyruvic acid is not the first oxidation product of phenylalanine, but oxidation takes place, probably, first in the benzene nucleus. It was found, in fact, that *dl*-phenylalanine, when perfused through the liver, gives rise to the normal *l*-tyrosine. From this, *p*-hydroxyphenylpyruvic acid could be formed, which is an acetoacetic acid former. It is suggested that when phenylpyruvic acid is burnt in the organism, it is converted first into phenylalanine, as it is known that the change of amino- into keto-acids in the body is a reversible one. S. B. S.

The Relations between Constitution and [Physiological] Action in Alicyclic Tetrahydro-β-naphthylamine and its Derivatives. MAX CLOETTA and ERNST WASER (*Arch. expt. Path. Pharm.*, 1913, **73**, 398—435).—From the substance mentioned, optically active *d*- and *l*-bases can be isolated, which resemble the racemic base in their action. From the latter a series of salts can be prepared with differing dissociation capacities, but no relation was found between this property and toxicity. The monomethyl derivative, like the original base, dilates the pupil, and raises body temperature and blood-pressure; the corresponding monoethyl compound acts in the same way, but is more toxic. If, however, the nitrogen is replaced by an acid residue (acetyl, formyl), the actions are reversed, the pupil is narrowed, and body temperature and blood-pressure fall. If an acid and alkyl group are both introduced there is a double action; for instance, in the frog, myosis is produced by the acid group, and in the rabbit, mydriasis by the alkyl group. In the case of derivatives that raise the blood-pressure, a second injection is not effective in the same way. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

The Fermentation of Pyruvic Acid by Bacteria. LÁSZLÓ KARCZAG and L. MÓCZÁR (*Biochem. Zeitsch.*, 1913, **55**, 79—87).—The bacteria which are capable of fermenting dextrose with evolution of gas are also able to ferment pyruvic acid. Amongst such bacteria are *B. coli*, *B. paratyphi-B.*, and Gaertner's bacillus. The gas evolution with bacteria follows more rapidly than with yeast, but there is a marked difference between the two classes of fermentations, for whereas with yeast the gas evolved is carbon dioxide, the pyruvic acid yielding this gas and formaldehyde, the gas evolved by bacteria consists for the most part of hydrogen. S. B. S.

Formation of Hydrogen Cyanide from Proteins. H. W. EMERSON, HAMILTON P. CADY, and E. H. S. BAILEY (*J. Biol. Chem.*, 1913, **15**, 415—418).—Certain micro-organisms (*B. pyocyaneus*) evolve hydrogen cyanide when grown on protein media, especially if the medium is slightly acid to litmus and phenolphthalein. This is absent when free mineral acid is present. W. D. H.

Formation of Hydrogen Cyanide from Proteins. B. J. CLAWSON and C. C. YOUNG, (*J. Biol. Chem.*, 1913, **15**, 419—422).—*B. pyocyaneus*, *B. fluorescens*, *B. violaceus*, and other bacteria the nature of which is still uncertain, produce hydrogen cyanide from protein material. W. D. H.

Chemistry of Bacteria. SAKAE TAMURA (*Zeitsch. physiol. Chem.*, 1913, **87**, 85—114).—Chemical investigations were made on large

quantities of the cells of *Bacillus tuberculosis* and *Mycobacterium lacticola perrugosum*. Extraction with ether failed to give any phosphatides, but treatment with warm alcohol showed the presence of a diaminomonophosphatide in each species of bacteria. Both cultures were found to contain an alcohol ($C_{29}H_{56}O$), for which the name *mycol* is suggested. This alcohol is present in the bacterial cell partly as an ester of a higher fatty acid, and it is to the alcohol or its ester that the acid- and alkali-resistance and gram-positiveness of the organisms are due. Adenine and hypoxanthine were present in each case, in addition to arginine, histidine, lysine, phenylalanine, proline, valine, tyrosine, and tryptophan. Bacterio-proteins are characterised by a high phenylalanine content.

H. B. H.

Fermentation of Cellulose by Thermophilic Bacteria. HANS PRINGSHEIM (*Centr. Bakt. Par.*, 1913, ii, **38**, 513—516).—Impure cultures of anaerobic, thermophilic, cellulose-decomposing bacteria were obtained from soil and horse manure. By means of a special apparatus the cultures were maintained at 55—60°, and samples of the decomposition gases were withdrawn from time to time. These were found to consist of 22—49% carbon dioxide, and the residue in all cases proved to be hydrogen.

Examination of the residual liquid cultures showed the presence of formic and acetic acids, but no butyric acid. This is significant, as the latter is the chief product of anaerobic cellulose decomposition at normal temperatures. Three grams of cellulose led to the production of 0·2125 gram of formic acid, 1·15 gram of acetic acid, a trace of lactic acid, and a mixture of carbon dioxide and hydrogen in the above proportions. H. B. H.

The Enrichment of the Invertase Content of Living Yeasts. LEOPOLD LICHTWITZ (*Biochem. Zeitsch.*, 1913, **56**, 160—162).—The author replies to certain criticisms of Meisenheimer, Gambarjan, and Semper (this vol., i, 1139), who found that the invertase content of yeast increases when the organism is kept in sugar solution. This is the direct contrary of what was found by the author. He calls attention to the fact, however, that yeast sown in large quantities in sugar solution, as was done by Meisenheimer and his collaborators, does not increase; on the contrary, it probably autolyses. This did not happen in the author's own experiments; hence, probably, the difference in the results. S. B. S.

Catalysts of Alcoholic Fermentation. HANS VON EULER (*Zeitsch. physiol. Chem.*, 1913, **87**, 142—144).—Earlier work has shown that the rapidity of fermentation by living yeasts is accelerated by the addition of alkali salts of organic and especially fatty acids, and dried yeast or yeast juice is not affected in a similar manner. Of the two possible interpretations of the results, particular attention has been paid to that which assumes that the activation is not directly connected with enzymes in the yeast cell, and experiments have been made to determine an alteration

of the protoplasmic layer of the cell or of the cell wall generally by the salts, with adsorption and an alteration of surface tension.

Preliminary experiments with sodium and ammonium salts of the acids having given negative results, an attempt was made to determine the action of various dye salts on the living cell. According to their behaviour towards the yeast cell, it was possible to divide the dye salts into three classes, namely, those without action on the cell, those which are clearly adsorbed, and others the entrance of which into the cell depends on the fermentative activity of the latter. These phenomena and the part played by an alteration of the surface tension are being further investigated.

H. B. H.

Influence of Certain Inorganic Salts, particularly Stannous Chloride and Bismuth Subnitrate, on Fermentation. GILBERT GIMEL (*Bull. Assoc. chim. Sucr. Dist.*, 1913, **31**, 128—129).—Results of further experiments confirm those obtained previously by the author (A., 1909, ii, 171). The activity of various yeasts in sweet worts is increased when the latter contain from 50 to 100 mg. of stannous chloride per litre. Bismuth subnitrate is soluble in acid liquids, such as musts, etc., and has a decided influence on the fermentation; it appears to inhibit acetic fermentation. The use of pure yeast cultures and different conditions of fermentation are probably the reason of the opposite opinion arrived at by Pozzi-Escot (this vol., i, 1139). W. P. S.

Protein Degradation in Yeast. I. The Influence of Sugar Fermentation on the Protein Degradation of Yeast. W. ZALESKI and W. SCHATALOV (*Biochem. Zeitsch.*, 1913, **55**, 63—71).—Various views have been expressed to explain the fact that proteolysis is less in yeast that has been used for sugar fermentation than in unused yeast, the Ivanov has stated that acetaldehyde is the fermentation product which is responsible for the antiproteolytic action. This statement the authors have been unable to confirm, for they find that an appreciable inhibition of yeast autolysis only takes place in concentrations of this aldehyde which are far higher than those found in fermentation liquors. The same is also true for furfuraldehyde and for formaldehyde, which latter, however, has a much stronger inhibitory action than acetaldehyde. Although the distillates from fermentations possess antiproteolytic properties, the actual antiproteolytic substance has not been isolated. The conditions of nutrition of the yeast exert some action on the subsequent proteolysis. The addition of amino-acids to yeasts increases the autolytic degradation of their proteins; it cannot be claimed, however, that they antagonise the antiproteolytic properties of the fermentation products. S. B. S.

Biochemical Conversion of Betaine into Glycollic Acid. FELIX EHRLICH and FRITZ LANGE (*Ber.*, 1913, **46**, 2746—2752).—In the course of their experiments on the behaviour of amino-acids towards micro-organisms, the authors have examined betaine, which is remarkably stable, not only to concentrated sulphuric acid or

qua regia at high temperatures, but also during passage through the bodies of most animals except the ruminants. They find that betaine is not assimilated by brewers' and distillers' yeasts or by various kinds of *Saccharomyces*, but is extensively degraded by *Willia anomala*, *Pichia farinosa*, *Pichia membranefaciens*, and other yeasts rich in oxydases; also many moulds, such as *Penicillium*, *Aspergillus*, *Monilia*, *Oidium*, and *Dematium*, are able to employ betaine for the formation of their albumin. In most cases characteristic degradation products of betaine cannot be isolated, partly because the decomposition is too extensive, partly owing to the difficulty of separating the decomposition products of the sugar added as a source of carbon. In experiments on solutions containing betaine, nutrient salts, and ethyl alcohol as a source of carbon, the authors find that after the addition of a pure culture of *Willia anomala* and keeping for eight weeks, glycollic acid is present in quantity sufficient for isolation; the amount is small, because the acid is an intermediate, not the final, product of the assimilation of the betaine. This is proved by the fact that *Willia anomala* grows extensively in a solution containing nutrient salts, and glycollic acid and carbamide as the only sources of carbon, the glycollic acid disappearing completely after four months; in a similar experiment, in which carbamide is the only source of carbon, growth of the yeast cannot be detected.

In the preceding experiments with betaine, not a trace of trimethylamine can be detected. Probably it is converted into methyl alcohol and ammonia, the latter, which also cannot be detected, being utilised by the organism in the formation of albumin.

In conclusion, the authors reply to Stoltzenberg (this vol., i, 345; compare also Ehrlich, A., 1912, i, 835; Stoltzenberg, *ibid.*, i, 380) concerning the isolation of betaine from molasses residue.

C. S.

Protein Synthesis in Plants. I. Protein Synthesis in the Bulbs of Allium cepa. W. Zaleski and W. Shatkin (*Biochem. Zeitsch.*, 1913, **55**, 72—78).—Experiments confirm a former statement of Zaleski, that the proteins increase in quantity in the injured bulbs when left in a moist atmosphere or in intact bulbs when allowed to grow in the dark. Estimations were of the total nitrogen, proteins, peptones, ammonia, acid amides, organic bases, and monoamino-acids. It was found, as a result, that the proteins are formed at the expense of the monoamino-acids. The mono- and di-amino-acids and ammonia were also estimated in the various specimens after hydrolysis with acids. The results obtained indicate that the monoamino-acids pre-existing combine with the pre-existing proteins. There is no evidence that the acid amides, without further change, take any direct part in the protein synthesis.

S. B. S.

The Inulin Metabolism of Cichorium intybus (Chicory). III. Viktor Grafe and Valentin Vouk (*Biochem. Zeitsch.*, 1913, **56**, 249—257. Compare A., 1912, ii, 977; this vol., i, 148).—It is shown

that by the freezing of the roots, the amount of inulin decreases, whereas the amount of reducing sugar increases; the amount of the latter returns to normal when the frozen roots are afterwards kept at normal temperature, whereas the amount of inulin remains unchanged. These results confirm the theory of Molisch, that the dissolved inulin acts as a "thermically active" protector against cold. The changes in the inulin and reducing sugar distribution in the roots which had wintered in a normal manner were also investigated. It was found that a hydrolysis of inulin takes place before new parts of the plants are visible; the reserve substances appear to be converted into building material, and this allows the further hydrolysis of the inulin reserves. A résumé of the results obtained by the authors up to the date of publication is also given. S. B. S.

The Colorimetric Method for Determining Hydrocyanic Acid in Plants with Special Reference to Kafir Corn. C. K. FRANCIS and W. B. CONNELL (*J. Amer. Chem. Soc.*, 1913, **35**, 1624—1628).—After examining the various methods for the estimation of small quantities of hydrocyanic acid, the authors decide in favour of a colorimetric process depending on the formation of ferric thiocyanate. This method indicates that Kafir corn contains minute quantities of combined hydrocyanic acid, the quantity apparently being greater in frost-bitten or stunted plants than in normal ones.

It is difficult to decide from the results whether the quantity of hydrocyanic present could prove fatal to an animal fed with this material. D. F. T.

Antitoxic Action of Chloral Hydrate on Copper Sulphate for Pisum sativum. R. P. HIBBARD (*Centr. Bakt. Par.*, 1913, ii, **38**, 302—308).—Water culture experiments in which garden peas were supplied with solutions of copper sulphate in concentrations varying from $M 3\times10^{-4}$ to $M 2{\cdot}5\times10^{-6}$, and with chloral hydrate, $M/165{\cdot}5$ to $M/16{,}550$, both together and separately. After forty-eight hours the roots of the plants were measured. Whilst in the single solutions growth was very slight, when both substances were supplied simultaneously the growth was distinctly better, especially when both substances are present in about equal amounts. The action of chloral hydrate in diminishing the toxicity of copper sulphate is similar, although less marked, to the influence of calcium over magnesium salts.

Several explanations are suggested, the most important of which is perhaps connected with the extent of ionisation which may be retarded when both substances are present. Or, changes may be brought about in the plasma membrane which will modify the permeability of the limiting layer. Then, again, the effect may be the result of changes in the cell itself. N. H. J. M.

Organic Chemistry.

Separation of Mixtures of a Saturated with an Unsaturated Hydrocarbon by means of Permanganate. S. S. NAMETKIN (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1423—1429).—Attempts to determine the proportions of the constituents of mixtures of (1) *cyclo*hexane and *cyclo*hexene, and (2) *n*-hexane and hexylene by oxidising the unsaturated hydrocarbon by means of permanganate were unsuccessful, owing to the saturated constituent reacting to some extent with the oxidising agent.

A similar method was then applied to analogous mixtures of gaseous hydrocarbons. For this purpose a special gas pipette was devised which permits the gaseous mixture to be passed repeatedly in small bubbles through the reagent, and in which the latter does not come into contact with mercury. After the reaction with saturated permanganate solution, the excess of oxidising agent was destroyed by means of saturated bisulphite solution, both this and the permanganate solution having been previously saturated with the saturated constituent of the gaseous mixture. With various mixtures of propane and ethylene, propane and propylene, and *cyclo*propane and propylene, the greatest error in the volume of the gas remaining after treatment with permanganate was 0·27%.

The unsatisfactory results obtained by Kishner (this vol., i, 153) are largely explained by the fact that, in most cases, the reaction was completed at 100°, and hence under conditions which should lead to attack of the saturated hydrocarbon. T. H. P.

Investigations on Polymerisation. I. Diethylene Hydrocarbons. SERGEI V. LEBEDEV and (in part) B. K. MERESHKOVSKI (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1249—1388. Compare A., 1911, ii, 774, 959; 1912, i, 173).—The vast majority of organic compounds are essentially unstable, and their great variety owes its existence to what the author terms passive resistance. It is quite conceivable that polymerisation, as a process directing molecules into more stable forms, is very widespread, and that most unsaturated organic compounds are able to polymerise under suitable conditions. No sharp line can be drawn between association and polymerisation, although with typical association no difference can be found between the chemical reactions of the monomeride and of the polymeride; it may be that, owing to ready dissociation of the latter, only the former reacts or that no sufficiently sensitive reagent for the polymeride has been discovered. The stability of the complex molecule depends on the particular type of polymerisation occurring, in addition to the properties of the individual compound.

In the great majority of cases polymerisation occurs with formation of a ring system, the ring having in all cases an even number of atoms. In studying polymeric changes, account must be taken of the isomerisa-

tion so common with unsaturated compounds, especially with rise of temperature.

Among the hydrocarbons the principal well-defined types of polymerisation are: (1) the styrene type, peculiar to ethylenic hydrocarbons with unsymmetrical substitution of the hydrogen atoms by definite groups (phenyl), and yielding polymerides of high molecular weight and structures not yet definitely established; (2) the stilbene type, exhibited by ethylene derivatives with symmetrical replacement of the hydrogen atoms by certain groups (phenyl); (3) the acetylene type, giving benzene derivatives; (4) the allene type, yielding *cyclo*butane derivatives; (5) the divinyl [$\Delta^{\alpha\gamma}$-butadiene] type, which forms *cyclo*hexane derivatives and polymerides of uncertain constitution. If it can be shown that stilbene forms a polymeride and styrene a dimeride of closed-chain structure, types (1) and (2) may have to be regarded as a single type; and, further, the resemblance between polymerides of the styrene and divinyl types (compare Ostromisslenski, A., 1912, i, 280) may lead to the fusion of these two types. Most cases of polymerisation of unsaturated compounds containing halogen, nitrogen, oxygen, or sulphur may be referred to one of the above types.

Polymerisation of the divinyl or $\Delta^{\alpha\gamma}$-butadiene type is first considered, an account being given of all such hydrocarbons studied in this respect. Experiments with isoprene and with di*iso*propenyl [$\beta\gamma$-dimethyl-$\Delta^{\alpha\gamma}$-butadiene] show that: (1) the relative proportions of dimeride and polymeride formed increase and diminish respectively as the temperature is raised; (2) at constant temperature, the ratio between the proportions of dimeride and polymeride does not change during the heating; (3) the reaction of polymerisation is sensitive to catalytic action, since replacement of the air in the tube by nitrogen results (with $\beta\gamma$-dimethyl-$\Delta^{\alpha\gamma}$-butadiene) in a fall of the relative amount of polymeride from 23% to 16·4%. It is further found that symmetrical hydrocarbons of this type, such as $\Delta^{\alpha\gamma}$-butadiene and its $\beta\gamma$-dimethyl derivative, yield a single dimeride, whereas the unsymmetrical isoprene gives two dimerides. In contradiction to the statement of Kondakov ("Synthetic Caoutchouc, its Homologues and Analogues," Yuriev, 1912, p. 101) and of Harries (A., 1911, i, 798), it is found that polymerisation of the pure hydrocarbons, without catalyst, yields no open-chain dimeride.

In general, it seems that no such equilibrium as that represented by dimeride $\rightleftharpoons$ monomeride $\rightleftharpoons$ polymeride exists, but that the processes of polymerisation are irreversible and proceed simultaneously in two directions, yielding dimeride and polymeride respectively. The existence of reversible processes of formation of dimeric and of polymeric forms renders it probable that such equilibria may yet be realised.

The possible methods of formation and structures of dimerides and polymerides are discussed in detail.

The dimeride of di*iso*propenyl [$\beta\gamma$-dimethyl-$\Delta^{\alpha\gamma}$-butadiene] is 4:6-dimethyldipentene or 4:6-dimethyl-$\Delta^{6,8(9)}$-menthadiene,

$$CMe{<}{\substack{CMe\cdot CH_2\\ CH_2\cdot CH_2}}{>}CMe\cdot CMe{:}CH_2,$$

which is a colourless liquid with an aromatic odour, b. p. 85°/13 mm.,

205·75?mm., D_4^{0} 0·8741, D_0^{20} 0·8597, $n_c^{19·7}$ 1·47716, n_D 1·48074, n_F 1·48796, n_G 1·49491 (compare Richard, A., 1911, i, 733). Treatment with ozone in chloroform solution at $-20°$ yields the *ozonide*, $C_{12}H_{20}O_6$, which is a froth-like, amorphous compound, exploding violently on heating, but failing to yield the triketone on decomposition with water. Oxidation of the dimeride in aqueous acetone by means of permanganate yields: (1) δ-*Methyl*-δ-iso*propenyl*-βη-*octandione*,

$$\mathrm{CH_3\cdot CO\cdot CH_2\cdot CMe(\cdot CMe{:}CH_2)\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3},$$

which is a viscous liquid, b. p. 132—133°/8·5 mm., and yields the *semicarbazone*, $C_{11}H_{20}O_2N_6$, m. p. 228°; hydrogenation of the diketone at the ordinary temperature in presence of platinum black gives δ-*methyl*-δ-iso*propyl*-βη-*octandione*, $\mathrm{CH_3\cdot CO\cdot CH_2\cdot CMePr^{\beta}\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3}$, as a colourless, viscous liquid, b. p. 133—135°/8 mm., D_4^{20} 0·9934, the corresponding *semicarbazone*, m. p. 202°, being also prepared. (2) A small proportion of an acid, m. p. 154—166°, containing 63·2% of carbon and 8·88% of hydrogen.

Oxidation of the dimeride of βγ-dimethyl-$\Delta^{\alpha\gamma}$-butadiene by means of benzoylhydroperoxide in ethereal solution (compare Prileschaev, A., 1911, i, 255) yields (1) a small proportion of the *monoxide*,

$$\mathrm{CMe}{\ll}\begin{matrix}\mathrm{CMe\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{CMe\cdot CMe}{<}\begin{matrix}\mathrm{CH_2}\\ \mathrm{O}\end{matrix},$$

b. p. 94—95°/10 mm., and (2) the *dioxide*, $C_{12}H_{20}O_2$, b. p. 110—112°/10 mm., which when heated in a sealed tube at 115° with water acidified with benzoic acid gives the tetrahydric alcohol (4:6-*limonetritol*), $\mathrm{OH\cdot CMe}{<}\begin{matrix}\mathrm{CMe(OH)\cdot CH_2}\\ \mathrm{CH_2{-}{-}{-}CH_2}\end{matrix}{>}\mathrm{CMe\cdot CMe(OH)\cdot CH_2\cdot OH}$, as a highly viscous liquid; oxidation of this by means of aqueous permanganate gave a small yield of the *keto-glycol*,

$$\mathrm{OH\cdot CMe}{<}\begin{matrix}\mathrm{CMe(OH)\cdot CH_2}\\ \mathrm{CH_2{-}{-}{-}CH_2}\end{matrix}{>}\mathrm{CMe\cdot COMe},$$

m. p. 155—165°.

The action of dry hydrogen chloride on the dimeride in carbon disulphide yields 1:2:4-*trimethyl*-4-*chloro*iso*propyl*-Δ^1-cyclo*hexene*, $\mathrm{CMe}{<}\begin{matrix}\mathrm{CMe\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{CMe\cdot CMe_2Cl}$, which is a colourless liquid, b. p. 122—124°/17 mm.

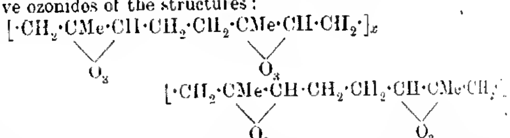
The polymeride of di*iso*propenyl is shown by means of its ozonide to have the structure $\mathrm{(\cdot CH_2\cdot CMe{:}CMe\cdot CH_2\cdot CH_2\cdot CMe{:}CMe\cdot CH_2\cdot)_x}$. The *ozonide*, $C_6H_{10}O_3$, separates partly in a gelatinous form and yields acetonylacetone when heated with water (compare Harries, A., 1911, i, 798).

Further details are given of the results obtained with isoprene (compare A., 1911, i, 26). For obtaining pure isoprene use was made of the following method elaborated in Favorski's laboratory and not yet published. Crude isoprene, b. p. 30—40°, obtained by decomposition of turpentine, is poured into a cooled solution of hydrogen bromide in acetic acid, and the precipitated mixture of bromides washed and dried. Amyl bromide is distilled off at 52—53° under 100 mm. pressure, and the residual αγ-dibromo-γ-methylbutane, after distillation at 80—82° under 23 mm. pressure, heated at 150° with a large excess

of pounded potassium hydroxide in a flask provided with a dephlegmator and condenser; the dibromide and monobromide formed from it are arrested by the dephlegmator and fall back into the flask, whilst the isoprene passes over and is condensed. The isoprene thus obtained, distilled over sodium, has b. p. 34·5—35°, D_0^{20} 0·6803, n_D^{20} 1·42207, n_C 1·41787, n_F 1·43307, n_G 1·44280, optical exaltation (D) 1·07 (compare Harries and Neresheimer, A., 1911, i, 798).

Two dimerides of isoprene were obtained: (1) Dipentene, b. p. 58°/9·5 mm., 174—175°/760 mm., D_0^0 0·8607, D_0^{20} 0·8454, $n_D^{19.7}$ 1·47428, n_C 1·47069, n_F 1·48211, n_G 1·48887. (2) 1 : 3-Dimethyl-3-ethenyl-Δ^6-*cyclo*hexene (*loc. cit.*), D_0^0 0·8481, $n_D^{19.7}$ 1·46581, n_C 1·46230, n_F 1·47294, n_G 1·47964, which yields a liquid tetrabromide, not obtained pure, and combines with 2HBr in acetic acid solution, giving the *compound*, $C_{10}H_{18}Br_2$, softening at 25° and melting at 34—35°. 1 : 3-Dimethyl-3-ethyl*cyclo*hexane (*loc. cit.*), obtained by hydrogenation of this dimeride in presence of platinum black and under a pressure of 70 atmospheres, has D_4^0 0·8132, D_4^{20} 0·7990, n_D^{20} 1·44112. The *ozonide*, $C_{10}H_{16}O_6$, of this dimeride resembles those of di*iso*propenyl and dipentene and, on decomposition, gives an oil resolved on boiling into the *ketodialdehyde*, $COMe{\cdot}CH_2{\cdot}CMe(CHO){\cdot}CH_2{\cdot}CH_2{\cdot}CHO$, which yields α-methyl-α-acetonylglutaric acid on oxidation. Treatment of the dimeride with benzoylhydroperoxide yields (1) the monoxide, which is a liquid, b. p. 68—70°/15 mm., with a camphor-like odour, and (2) the *dioxide*, $O{<}\begin{array}{l}CMe{-}{-}{-}CH_2\\ |\\ CH{\cdot}CH_2{\cdot}CH_2\end{array}{>}CMe{\cdot}CH{<}\begin{array}{l}O\\ |\\ CH_2\end{array}$, which is a liquid with an aromatic odour, b. p. 108—109°/15 mm., and yields the *compound*, $C_{10}H_{20}O_4$, on hydration.

Two isomeric polymerides of isoprene are possible theoretically, and should give ozonides of the structures:

(1) 

and (II)

Of these, (1) corresponds with natural caoutchouc and should give, on decomposition, lævulinaldehyde and its peroxide, and lævulic acid; all these products were actually observed. Similarly, (II) should give succindialdehyde, succinic acid and acetonylacetone, none of which could be detected. Hence, only the former polymeride is formed; its *ozonide*, $C_5H_8O_3$, is an extremely viscous liquid, exploding when heated.

Piperylene should yield, not a dimeride of the structure,

$$CMe{<}\begin{array}{l}CH{-}CH_2\\ CH_2{\cdot}CH_2\end{array}{>}CH{\cdot}CH{:}CHMe$$

(compare Harries, this vol., i, 284), but two dimerides, formed thus:

$$(1)\quad CH_3{\cdot}\underset{|}{C}H{\cdot}\underset{|}{C}H{\cdot}\underset{|}{C}H{\cdot}CH_2{\cdot} \longrightarrow CH{<}\begin{array}{l}CH{-}{-}CH_2\\ CHMe{\cdot}CH_2\end{array}{>}CH{\cdot}CH{:}CHMe,$$

$$\text{and (2)}\quad \begin{array}{l}CH_3\\ |\\ CH{\cdot}CH{\cdot}CH{\cdot}CH_2\\ \;\;\;\;\;\;\;|\;\;\;\;\;\;|\;\;\;\;\;\;|\end{array} \longrightarrow CH{<}\begin{array}{l}CH{-}CHMe\\ CH_2{\cdot}CHMe\end{array}{>}CH{\cdot}CH{:}CH_2;$$

the former should have the higher boiling point.

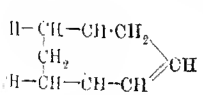
According to a private communication from Favorski, di*iso*crotyl [$\beta\epsilon$-dimethyl-$\Delta^{\beta\delta}$-hexadiene] undergoes spontaneous change into a waxy substance, but this was not observed by the author. This hydrocarbon undergoes polymerisation with great difficulty, only 50% of it being transformed after being maintained at 290° for ten days. The employment of such a high temperature causes partial isomerisation of the dimeride, of which only a single one should be formed from a symmetrical molecule, and also results in decomposition of the polymeride. The dimeride is 3 : 3 : 5 : 5 : 6 : 6-*hexamethyl*-4-*iso**crotyl*-Δ^1-*cyclohexene*, $CH{<}{\genfrac{}{}{0pt}{}{CH{-}{-}CMe_2}{CMe_2{\cdot}CMe_2}}{>}CH{\cdot}CH{:}CMe_2$, b. p. 130—132°/24 mm., D_4^0 0·8634, D_4^{20} 0·8491, n_D^{20} 1·47751, n_C 1·47452, n_F 1·48757, n_G 1·49120. The polymeride was obtained only as an impure, yellow, viscous liquid containing decomposition products.

Myrcene, which probably consists of a mixture of two or more isomerides, was found to have the constants: b. p. 56—57°/12 mm., D_4^{20} 0·7982, n_D^{20} 1·47065, n_C 1·46675, n_F 1·48055, n_G 1·48905. When heated for twelve days at 150°, it yields (1) two cyclic isomerides of myrcene. (*a*) b. p. 60—61·5°/16 mm., D_4^{20} 0·8392, n_D^{20} 1·46611, n_C 1·46270, n_F 1·47334, n_G 1·47974, and (*b*) b. p. 65—65·5°/16 mm., D_4^{20} 0·8340, n_D^{20} 1·47133, n_C 1·46774, n_F 1·47922, n_G 1·48613; (2) a dimeride, b. p. 183—184°/10 mm., D_4^{20} 0·8763, $n_D^{20 \cdot 1}$ 1·49859, n_C 1·49568, n_F 1·50668, n_G 1·51606; (3) a viscous polymeride yielding a mixture of products when treated with ozone (compare Harries, A., 1902, i, 811).

α-Phenyl-$\Delta^{\alpha\gamma}$-butadiene polymerises with great ease. The dimeride was investigated by Riiber (A., 1904, i, 569), who suggested formulæ for it and for the tribasic acid yielded on oxidising it with permanganate. The author regards these formulæ as inaccurate, since, according to his scheme, the dimeride should have the structure

$$CH{<}{\genfrac{}{}{0pt}{}{CH{-}{-}{-}CH_2}{CHPh{\cdot}CH_2}}{>}CH{\cdot}CH{:}CHPh,$$

and the tribasic acid, $CO_2H{\cdot}CHPh{\cdot}CH_2{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CO_2H$, the latter agreeing better with the analytical data than that proposed by Riiber.



As was shown by Stobbe and Reuss (A., 1912, i, 842), *cyclo*pentadiene polymerises so rapidly that intense cooling is necessary in order to obtain it in the monomeric form. If the type of polymerisation exhibited by open-chain hydrocarbons holds also for cyclic compounds, the dimeride should have the annexed structure (compare Kraemer and Spilker, A., 1896, i, 289). This case is under investigation.

Allene hydrocarbons polymerise with great ease and, unlike those of the divinyl type, with velocities varying only within narrow limits. The character of the polymerisation is also different, the polymerides being *cyclo*butane derivatives and forming an uninterrupted series from di- to hexa-merides. Actually, however, the polymerisation of allene hydrocarbons is complicated by transformation to the type shown by those of the divinyl series. This occurs in two ways: (1) the allene hydrocarbons undergo isomeric change into divinyl derivatives with

comparative ease, and (2) the dimerides are cyclic derivatives of divinyl; thus, that of allene has the structure

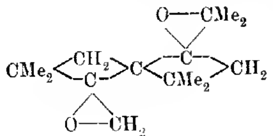
$$\mathrm{CH_2{:}C}<\begin{matrix}\mathrm{-CH_2-}\\ \mathrm{C(:CH_2)}\end{matrix}>\mathrm{CH_2},$$

and readily polymerises giving a di-dimeride and a polymeride. At the ordinary temperature allene hydrocarbons polymerise so slowly that years elapse before the formation of an appreciable proportion of polymeride. But the temperature-coefficient of the velocity of the change is far greater than with divinyl derivatives, and at 150° the velocity is approximately the same as with isoprene and di*iso*propenyl. The author elaborates a scheme to explain the mechanism of the process, starting from the assumptions that the molecules combine initially at a single point and that the union is directed by two causes: the magnitude of the affinity with the unsaturated atoms and the polarity. The construction of models of the polymeric forms shows that two types of arrangement in space are possible: (1) the cyclic type, in which the central carbon atoms of allene are arranged in a ring in one plane, with the four-membered rings alternately on either side of this basal plane; and (2) the spiral type, in which the central atoms of the allene groups are arranged in a spiral so that the first, fourth, and seventh carbon atoms occupy analogous positions on the spiral, and so on; the four-membered rings lie in three mutually perpendicular planes, the first, fourth, and seventh rings also taking up similar positions on the spiral. The dimerides of the two types are identical, as also are the trimerides. Stereoisomerism is possible, beginning with the tetrameride, and assuming the formation of polymeric forms according to both types, two stereoisomerides may be expected for the tetra-, penta-, and hexa-meride. Higher degrees of polymerisation are possible only with the spiral type.

When heated to 130—140°, *as*-dimethylallene gives 3% of dimeride, b. p. 140—141°, 18% of dimeride, b. p. 149—150°, 40% of dimeride, b. p. 179—181°, 33% of trimeride, b. p. 100°/8 mm., and 6% of vaseline-like residue. The three dimerides, which are the only possible ones, have been already described (A., 1912, i, 173). The *trimeride*,

$$\mathrm{CMe_2}<\begin{matrix}\mathrm{-CH_2-}\\ \mathrm{C(:CH_2)}\end{matrix}>\mathrm{C}<\begin{matrix}\mathrm{C(:CMe_2)}\\ \mathrm{-CMe_2-}\end{matrix}>\mathrm{CH_2},$$

is a colourless, odourless liquid, b. p. 100°/8 mm., D_4^0 0·8723, D_4^{20} 0·8578, n_D^{20} 1·48724, n_C 1·48395, n_F 1·50260, n_G 1·51398, optical exaltation 2·28, and has the normal molecular weight in freezing benzene. Hydrogenation of the trimeride in presence of platinum black yields the *compound*, $\mathrm{CMe_2}<\begin{matrix}\mathrm{-CH_2-}\\ \mathrm{CHMe}\end{matrix}>\mathrm{C}<\begin{matrix}\mathrm{CHPr^\beta}\\ \mathrm{-CMe_2-}\end{matrix}>\mathrm{CH_2}$, b. p. 116—118°/23 mm., D_4^0 0·8521, D_4^{20} 0·8380, $n_D^{19\cdot9}$ 1·46362, n_C 1·46101, n_F 1·47274, n_G 1·47827, optical exaltation 1·50.



The ozonide of the trimeride is unstable, and was not obtained pure. Oxidation by means of benzoylhydroperoxide yields the *dioxide* (annexed formula), m. p. 49°, b. p. 137°/16 mm., which undergoes partial hydration to the *compound*, $C_{15}H_{26}O_3$, m. p. 136·5°.

probably a glyco-oxide. Attempts to complete the hydration by heating with water containing a trace of acid resulted in the formation of a *diketone*, $C_{15}H_{24}O_2$, m. p. 86°, which yields a *semicarbazone*,

$$C_{17}H_{30}O_2N_6,$$

m. p. 170° (decomp.), but was not obtained in sufficient quantity to admit of the determination of its structure.

[With B. K. MERESHKOVSKI.]—When heated in a sealed tube at 150°, trimethylallene undergoes polymerisation and isomerisation, the mixture of dimerides consisting principally of 1:2-*dimethyl*-3:4-*diisopropylidene*cyclo*butane*, $\begin{array}{l}CHMe\cdot C{:}CMe_2\\ |\qquad\quad\ |\\ CHMe\cdot C{:}CMe_2\end{array}$, which is a colourless liquid with the odour of kerosene, b. p. 69—70°/11 mm., 190—191°/754 mm., D_4 0·8217, n_D^{20} 1·48337, n_C 1·47946, n_F 1·49282, n_G 1·50297. The ozonide is unstable, and on distilling in a current of steam is decomposed into dimethylsuccinic acid, acetone peroxide, and 1:2-*dimethyl*-3-*isopropylidene*cyclo*butan*-4-*one*, $\begin{array}{l}CHMe\cdot C{:}CMe_2\\ |\qquad\quad\ |\\ CHMe\cdot CO\end{array}$, which is a colourless liquid with the characteristic quinone-like odour common to all unsaturated ketones obtained from dimerides of allene hydrocarbons, b. p. 83—86°/20 mm., and was not obtained free from traces of the original dimeride; its *semicarbazone*, $C_{10}H_{17}ON_3$, m. p. 200—201° (decomp.), contained a small proportion of another semicarbazone, m. p. about 180°; oxidation of the ketone with permanganate yields the maleinoid form of dimethylsuccinic acid. Products of higher polymerisation are formed to the extent of 10%, but no individual compounds were isolated.

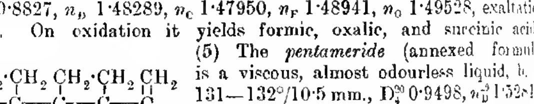
[With B. K. MERESHKOVSKI.]—At 150°, polymerisation of *s*-dimethylallene is complete in four to five days. The products contain (1) about 90% of the dimeride, 1:2-*dimethyl*-3:4-*diethylidene*cyclo*butane*, $\begin{array}{l}CHMe{:}C\cdot CHMe\\ \qquad\quad\ |\quad\ |\\ CHMe{:}C\cdot CHMe\end{array}$, which is a colourless liquid, b. p. 65°/22 mm., 163°/762 mm., D_4^{20} 0·8113, n_D^{20} 1·47850, n_C 1·47423, n_F 1·48913, n_G 1·49838, optical exaltation 2·25. When oxidised with permanganate, this dimeride yields the maleinoid form of *s*-dimethylsuccinic acid and acetic acid (?), whilst hydrogenation at ordinary temperature in presence of platinum black yields 1:2-*dimethyl*-3:4-*diethyl*cyclo*butane*, $\begin{array}{l}CHEt\cdot CHMe\\ |\qquad\quad |\\ CHEt\cdot CHMe\end{array}$, b. p. 155—156°/760 mm., D_4^{20} 0·7729, n_D^{20} 1·42447, n_C 1·42193, n_F 1·42950, n_G 1·43377, optical exaltation 0·24; (2) about 5% of the *trimeride*, $CHMe\!<\!\begin{array}{l}CHMe\\ C({:}CHMe)\end{array}\!>\!C\!<\!\begin{array}{l}C({:}CHMe)\\ CHMe\end{array}\!>\!CHMe$ (?), which is a colourless, odourless liquid, b. p. 108—116°/17 mm.

When heated at 140° for three and a-half days, allene yields 5% of dimeride, 15% of trimeride, 5% and 22% of tetramerides I and II, 18% of pentameride, 10% of hexameride, and 25% of residual polymeride. With the exception of the dimeride and tetrameride I, these polymeric forms all rapidly absorb atmospheric oxygen, and all without exception yield formic, oxalic, and succinic acids on oxidation, and give a dark brown coloration with tetranitromethane. The viscosity increases with the degree of polymerisation, the hexameride being somewhat more

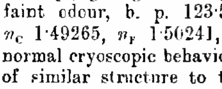
liquid than glycerol. (1) The dimeride, 1 : 2-*dimethylene*cyclo*butane*, $\begin{matrix} CH_2\cdot C{:}CH_2 \\ CH_2\cdot C{:}CH_2 \end{matrix}$, is a colourless liquid, b. p. 63—65°, $D_4^{\ }$ 0·76.., n_D^{20} 1·42317. (2) The *trimeride*, $CH_2{<}\begin{matrix} -CH_2- \\ C({:}CH_2) \end{matrix}{>}C{<}\begin{matrix} C({:}CH_2) \\ -CH_2- \end{matrix}{>}CH_2$, is a liquid with a peculiar odour, b. p. 135°/774 mm., 70·5°/90 mm., 38°/21 mm., D_4^{20} 0·8624, n_D^{20} 1·48064, n_C 1·47677, n_F 1·48922, n_G 1·49..., optical exaltation 1·04. It readily absorbs hydrogen in presence of platinum-black giving the *compound*,

$$CH_2{<}\begin{matrix} CH_2- \\ CHMe \end{matrix}{>}C{<}\begin{matrix} CHMe \\ CH_2- \end{matrix}{>}CH_2,$$

which is a colourless, almost odourless liquid, b. p. 132°/756 mm., D_4^{20} 0·7972, n_D^{20} 1·43459, n_C 1·43159, n_F 1·43950, n_G 1·44410, optical exaltation 1·23. (3) Tetrameride I is a *dimeride of the dimeride*, $\begin{matrix} CH_2\cdot C\cdot CH_2\cdot CH_2 \\ CH_2\cdot C\text{———}CH_2 \end{matrix}{>}C{<}\begin{matrix} -CH_2- \\ C({:}CH_2) \end{matrix}{>}CH_2$, and forms a colourless liquid with an odour of turpentine, b. p. 72—74°/9 mm., D_4^{20} 0·8..., n_D^{20} 1·50301, n_C 1·49905, n_F 1·51204, n_G 1·51999, optical exaltation 2·58. On prolonged heating in a sealed tube at 150°, it thickens and deposits an insoluble polymeride, which was obtained only in small amount. With hydrogen in presence of platinum-black, it gives the *compound*, $\begin{matrix} CH_2\cdot CH\cdot CH_2\cdot CH_2 \\ CH_2\cdot CH\text{———}CH_2 \end{matrix}{>}C{<}\begin{matrix} CH_2- \\ CHMe \end{matrix}{>}CH_2$, as a colourless liquid with a faint odour, b. p. 77—78°/13·5 mm., D_4^{20} 0·857., n_D^{20} 1·46809, n_C 1·46448, n_F 1·47305, exaltation 1·51. (4) *Tetra-*



meride II (I.) is a colourless liquid with an odour of kerosene, b. p. 101°/10 mm., D_4^{20} 0·9346, n_D^{20} 1·52624, n_C 1·52210, n_F 1·53579, n_G 1·54396, exaltation 2·33, and has the normal molecular weight in freezing benzene. On hydrogenation it yields the *compound* (II.), b. p. 95°/13·5 mm., D_4^{20} 0·8827, n_D 1·48289, n_C 1·47950, n_F 1·48941, n_G 1·49528, exaltation 2·02. On oxidation it yields formic, oxalic, and succinic acids. (5) The *pentameride* (annexed formula) is a viscous, almost odourless liquid, b. p. 131—132°/10·5 mm., D_4^{20} 0·9498, n_D^{20} 1·52814, n_C 1·52422, n_F 1·53765, n_G 1·54591, exaltation 2·90. On hydrogenation it takes up sufficient hydrogen to saturate two double linkings, giving the *compound*, $C_{15}H_{24}$, as a colourless liquid with a faint odour, b. p. 123·5—124·5°/8 mm., D_4^{20} 0·9152, n_D^{20} 1·4962., n_C 1·49265, n_F 1·50241, n_G 1·50810, exaltation 2·40, and exhibits normal cryoscopic behaviour in benzene. (6) The *hexameride*, $C_{18}H_{24}$, of similar structure to the foregoing, is a viscous, almost odourless liquid, b. p. 170°/10 mm., D_4^{20} 0·9721, n_D^{20} 1·53869, n_C 1·5342., n_F 1·54817, n_G 1·55648, exaltation 3·64. Oxalic and succinic acids were found among its products of oxidation.



It has been shown by Favorski (A., 1891, 1330) that, when heated with alcoholic alkali hydroxide, hydrocarbons of the diallyl series undergo isomeric change to divinyl derivatives: C:C·C·C·C:C → C·C:C·C:C·C; thus diallyl yields $\Delta^{\beta\delta}$-hexadiene. When heated at 250° for ten days, diallyl begins to isomerise, 10% of the monomeride boiling at a higher temperature than diallyl. The crude polymeride consists of (1) about 15% of a liquid of peculiar odour, b. p. 97—98°/20 mm., consisting of mixed dimerides, and (2) about 85% of colourless, insoluble, caoutchouc-like polymeride, which is converted into ozonide only with difficulty. At 150°, $\Delta^{\beta\delta}$-hexadiene yields a dimeride, b. p. 88—90°/20 mm., quite different from that of diallyl, but at 250° it gives a considerable proportion of the dimeride, b. p. 96—98°/20 mm.

The author has devised a method for determining the velocity at which polymerisation occurs. From 2 to 10 grams of the hydrocarbon were sealed in tubes and heated in a perfectly dark thermostat at 159 ± 0·1°. After definite intervals of time, the tubes were cooled and their contents introduced into tared distilling flasks connected with small condensers and tared receivers. Liquids with low boiling points were distilled at ordinary pressure and those with high boiling points under diminished pressure. A bath of Wood's metal was used for the heating, its temperature being at first below the boiling point of the monomeride, and finally about the boiling point of the dimeride. The monomeride, the residual polymeride, and sometimes also the dimeride were weighed to within 0·02 gram. In general, all the polymerised products were taken into account in calculating the velocity. The results obtained in this way were corrected for several errors inherent in the method. The numbers obtained with twelve hydrocarbons of the $\Delta^{\alpha\gamma}$-butadiene series show that: (1) With isomerides, the transference of a substituent from the extreme atom of a conjugated system of atoms to the middle atom is accompanied by increase in the velocity of polymerisation, and conversely. (2) The formation of a ring from a chain containing a conjugated system increases the velocity of polymerisation. (3) In homologous series, increase of the mass of a substituent at the middle (or extreme) atoms of a conjugated system increases (or lowers) the velocity of polymerisation, assuming that the heating occurs at corresponding temperatures. The results given by the four allene derivatives lead to the following conclusions: (1) The velocity of polymerisation of isomeric hydrocarbons of the allene series does not depend on the positions of the substituent groups. (2) In an homologous series of allene hydrocarbons, increase of the mass of the substituent results in increased velocity of polymerisation, the heating being at corresponding temperatures.

T. H. P.

Polymerisation as a Method of Detecting the Allene Group, C:C:C. SERGEI V. LEBEDEV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1390—1391).—The polymerisation of allene hydrocarbons affords a simple and easy method of distinguishing them from diethylenic hydrocarbons of other types. At 150° allene hydrocarbons are polymerised almost completely in one to two days, part undergoing isomeric change to $\Delta^{\alpha\gamma}$-butadiene derivative. The crude polymeride consists principally

of dimeride or, with unsymmetrical allene hydrocarbons, of dimerides. The dimeride is separated by distillation; when several are present, the predominating one is obtained by fractionation. The dimeride is of the type $\begin{matrix} C\cdot C:C \\ | \quad | \\ C\cdot C:C \end{matrix}$, and, on oxidation by means of permanganate in acetone solution, gives a good yield of succinic acid or one of its substituted derivatives, these being well crystallised and readily transformed into anhydrides. Further, the dimerides of allene hydrocarbons exhibit marked optical exaltation, which is usually about, and greater than, 2; dimerides from diethylene hydrocarbons of other types are optically normal. T. H. P.

Isomeric Transformations of Diethylenic Hydrocarbons. I. Isomeric Transformation of Dimethylallene [γ-Methyl-$\Delta^{\alpha\beta}$-butadiene] into Isoprene. L. M. KUTSCHEROV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1634—1654).—When heated with quinoline hydrobromide (compare Favorski and Borgmann, A., 1908, i, 15), γ-methyl-$\Delta^{\alpha\beta}$-butadiene readily undergoes isomeric change into isoprene (50—55% yield) and a small proportion of *iso*propylacetylene [γ-methyl-Δ^{α}-butinene]. The reaction is irreversible, neither isoprene nor γ-methyl-Δ^{α}-butinene undergoing isomerisation under the above conditions; isoprene yields condensation products and combines with the pyridine, whilst γ-methyl-Δ^{α}-butinene partly remains unchanged and partly undergoes conversion into an unsaturated derivative according to the equation: $C_5H_8 + C_9H_7N,HX = C_5H_9X + C_9H_7N$. The formation from γ-methyl-$\Delta^{\alpha\beta}$-butadiene of isoprene is represented by the scheme: $CMe_2:C:CH_2 + C_9H_7N,HX \longrightarrow CMe_2X\cdot CH:CH_2 + C_9H_7N \longrightarrow CH_2:CMe\cdot CH:CH_2 + C_9H_7N,HX$, and that of γ-methyl-Δ^{α}-butinene by: $CMe_2:C:CH_2 + C_9H_7N,HX \longrightarrow CHMe_2\cdot CX:CH_2 + C_9H_7N \longrightarrow CHMe_2\cdot C:CH$; in the former case, the compound $CMe_2X\cdot CH_2\cdot CH_2X$ may also be formed as an intermediate product.

β-Bromo-γ-methyl-Δ^α-butene, $CH_2:CBr\cdot CHMe_2$, formed by treating γ-methyl-Δ^{α}-butinene either with hot quinoline hydrobromide or with hydrogen bromide in the cold, is a liquid, b. p. 100·5°/758 mm., D_4^{20} 1·2381 (1·2320), n_D^{20} 1·45093 (1·45033), and is reconverted into γ-methyl-Δ^{α}-butinene when heated in a sealed tube with alcoholic potassium hydroxide at 138°. When treated with aqueous hydrobromic acid it yields: (1) $\gamma\delta$-dibromo-β-methylbutane, b. p. 61—62°/12 mm.; (2) *γγ-dibromo-β-methylbutane*, $CMeBr_2\cdot CHMe_2$, m. p. 13—15°, b. p. 53·5—54°/12 mm., 44—45°/8 mm., D_4^0 1·6987, D_4^{20} 1·6695, n_D^{20} 1·50468, which is converted into methyl *iso*propyl ketone when heated in a sealed tube with water and lead hydroxide.

γγδ-Tribromo-β-methylbutane, $CH_2Br\cdot CBr_2\cdot CHMe_2$, obtained by the action of bromine on β-bromo-γ-methyl-Δ^{α}-butene, is a hygroscopic liquid, b. p. 100—101·5°/12·5 mm., D_4^{20} 2·07112, n_D^{20} 1·55448.
T. H. P.

Pyrogenic Acetylene Condensations. RICHARD MEYER and AUGUST TANZEN (*Ber.*, 1913, **46**, 3183—3199. Compare A., 1912, i, 525).—The previous experiments in which nine hydrocarbons present in coal tar were obtained synthetically by the condensation of acetylene

have been repeated in an enlarged apparatus which enabled 6000 grams of tar to be obtained, which has been completely investigated. Phenanthrene and acenaphtheno and also, in small quantities, styrene and hexylene were identified. The last has previously only been found in boghead coal and in bituminous shale.

On heating acetylene diluted with coal gas with hydrogen cyanide, pyridine and its homologues were obtained. Mixtures of ammonia and benzene yield aniline when heated, the reaction being reversible. Further condensation of the aniline leads to carbazole and to benzonitrile, the latter being formed by the action of hydrogen cyanide on aniline.

In all, therefore, seventeen constituents of coal tar have been identified as formed by the pyrogenetic condensation of acetylene. The hexylene formed is *n*-hexylene, identical with that from mannitol.

The formation of pyridine requires a temperature of 800°, at which the mixture of acetylene, hydrogen, and hydrogen cyanide can be heated without catching fire. Apparently the hydrogen cyanide acts as a poison towards the catalytic changes which bring about the sudden decomposition of acetylene and cause a mixture of acetylene and hydrogen to catch fire much below 800°.

The apparatus used is figured and described in detail. E. F. A.

Improvements in the Preparation of Dichlorinated Hydrocarbons in which the Chlorine is Combined with Different Carbon Atoms. WILLIAM H. PERKIN, CHARLES WEIZMANN, and HAROLD DAVIES (Fr. Pat. 452503, and 1st Addition).—If vaporised hydrocarbons or chlorohydrocarbons are treated with the required halogen with or without the addition of a catalyst or in the presence of light with subsequent fractionation under diminished pressure definite products are obtained, and the preparation of the following compounds as chief products of the reaction is described.

From *iso*amyl chloride: *δ-dichloro-β-methylbutane* (b. p. 142°), *γδ-dichloro-β-methylbutane* (b. p. 150°), and *βδ-dichloro-β-methylbutane* (b. p. 170—172°).

From α-chlorobutane: tetrachlorobutane: from *n*-heptane: chloroheptane, and from *iso*amyl bromide: βδ-dichloro-β-methylbutane (b. p. 72—75°/5 mm.).

Monochloroacetic acid can also be prepared from acetic acid in a similar manner. F. M. G. M.

Compounds of Aluminium Bromide with Hydrogen Sulphide and Organic Bromides. Synthesis of Mercaptans. VLADIMIR A. PLOTNIKOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1162—1173. Compare A., 1907, i, 580).—The following compounds have been prepared: $AlBr_3,H_2S$, obtained by passing hydrogen sulphide through aluminium bromide, either in a fused condition or in solution in carbon disulphide, forms colourless crystals, m. p. about 84°, and is decomposed immediately by the moisture of the air with liberation of hydrogen bromide and hydrogen sulphide.

$AlBr_3,EtBr,H_2S$, obtained by passing hydrogen sulphide through a solution of aluminium bromide in ethyl bromide, forms snow-white

crystals, m. p. (in sealed capillary) about 81°, is readily decomposed by water with formation of mercaptan (90% yield): $AlBr_3,EtBr,H_2S$ + aq. = $AlBr_3$,aq. + EtHS + HBr, and in solution attacks aluminium or zinc with liberation of hydrogen. Electrolysis of a solution of the compound in ethyl bromide with platinum electrodes results in the development of hydrogen at the cathode and bromine at the anode.

$AlBr_3,CH_2Br\cdot CH_2Br,H_2S$ forms a pale yellow, crystalline powder decomposing at about 200°, and is also decomposed by the moisture of the air with formation of an oil with a garlic-like odour.

$AlBr_3,CHBr_3,H_2S$ is decomposed by water, apparently with formation of thioformic acid, which then undergoes condensation.

The structures of these compounds are considered in the light of Werner's co-ordination system. T. H. P.

Dipropyl*iso*amylcarbinol and the Action of Nickel Carbonate on its Chlorohydrin. IVAN VANIN (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1155—1162).—Zaicev (A., 1912, i, 777) has shown that the action of silver carbonate on 1-chloro-1-allyl*cyclo*hexane yields an unsaturated hydrocarbon, C_9H_{14}. The author finds that a similar change is effected by the action of nickel carbonate on ε-chloro-β-methyl-ε-propyloctane.

Dipropyl*iso*amylcarbinol (β-methyl-ε-propyloctan-ε-ol), obtained by the action of magnesium *iso*amyl bromide on butyrone, has properties agreeing well with those given by Murat and Amouroux (A., 1912, i, 527).

ε-Chloro-β-methyl-ε-propyloctane, $CPr_2Cl\cdot CH_2\cdot CH_2\cdot CHMe_2$, is a colourless, mobile liquid, b. p. 115—117°/30 mm., D_0^0 0·8901, D_0^{20} 0·8748. When heated with excess of nickel carbonate in a reflux apparatus in an oil-bath at 135—145° for four to five hours, it is converted into a *methylpropyloctene*, $CHEt\colon CPr\cdot CH_2\cdot CH_2\cdot CHMe_2$ or $CPr_2\colon CH\cdot CH_2\cdot CHMe_2$, b. p. 89—91°/20 mm., 189—191°/756·5 mm., D_0^0 0·7773, D_0^{20} 0·7610, which may be identical or isomeric with that obtained by Murat and Amouroux (*loc. cit.*) by catalytic dehydration of dipropyl*iso*amylcarbinol with alumina. T. H. P.

Transformation of *iso*Nitro-compounds into Ketones. S. S. NAMETKIN and (Mlle.) E. I. POZDNJAKOVA (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1420—1422).—Three methods exist for converting secondary nitro-compounds into ketones: (1) Reduction of nascent *iso*nitro-compounds by means of stannous chloride (compare Konovalov, A., 1899, i, 733); (2) action of acids on aqueous solutions of salts of *iso*nitro-compounds (compare Nef, A., 1895, i, 3); (3) heating of halogen-substituted nitro-compounds (compare Wislicenus and his collaborators, A., 1908, i, 973; 1909, i, 99; 1910, i, 621; 1912, i, 521). The last two methods are, however, only of theoretical interest. Nef's method yields, besides the ketone (or aldehyde), more or less free nitro-compound, which renders purification difficult, whilst method (3) is applicable only to those cases in which aggregation of several electro-negative groups to one carbon atom renders the halogen-

considered nitro-compound unstable. Konovalov's method gives excellent results.

Investigation of the action of permanganate on nitro-compounds (compare A., 1910, i, 830; Konovalov, A., 1904, i, 499; 1905, i, 762) shows that, under the following conditions, almost quantitative yields of the corresponding ketones are obtained. A solution of the nitro-compound in potassium hydroxide solution (1 part to 2 of water) is diluted with five to six times its volume of water, and in the event of separation of insoluble nitro-compound, the latter is extracted by means of light petroleum. To the aqueous solution, mixed with pieces of ice in a large flask, is gradually added the theoretical quantity of 1·5% potassium permanganate solution, the ketone being subsequently distilled in a current of steam.

In this way, nitro*cyclo*hexane gave a 97% yield of *cyclo*hexanone, and nitrofluorene, a 96% yield of fluorenone. T. H. P.

Structure of *iso*Nitro-compounds. S. S. Nametkin (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1414—1420).—The author criticises the arguments advanced by Steinkopf and Jürgens (A., 1912, i, 152) in support of Hantzsch's formula for *iso*nitro-compounds.

Stress is laid on the unsaturated character of these compounds, which react with halogens and halogen hydracids, and in alkaline solution, even in the cold, instantly reduce 1—2% potassium permanganate solution, the nitro-compounds being converted almost quantitatively into ketones (compare preceding abstract). Such ready oxidisability is difficult to explain according to Hantzsch's ring constitution, but is easily understood if the presence of a double linking is assumed as is the case in the structure proposed by Michael and Nef. If oxidation at a double linking between carbon and nitrogen follows the same course as at one between two carbon atoms, the initial product of the reaction should be a compound exhibiting an accumulation of hydroxyl groups and hence possessing but slight stability: loss of the elements of water from this compound would yield ketone and a nitrite: $\equiv C{:}NO{\cdot}OK \longrightarrow \equiv C(OH){\cdot}NO(OH)(OK) \longrightarrow \equiv CO + KNO_2 + H_2O$.

The behaviour of salts of primary nitro-paraffins on acidification, which yields transitory nitroso-compounds and finally hydroxamic acids, is also readily accounted for on the basis of Michael and Nef's formula: $CHR{:}NO{\cdot}OH \longrightarrow CHR{:}O + {:}NOH \longrightarrow CHR(OH){\cdot}NO \longrightarrow CR(OH){:}NOH$. When, however, the nitro group is accompanied by a more or less electronegative group, this intermediate formation of nitroso compound does not take place, as no blue or green coloration then makes its appearance. Such an essential variation in one and the same reaction leads the author to suggest that the first stage in the action of dry hydrogen chloride is most probably a direct combination, the unstable compound thus formed subsequently undergoing intramolecular rearrangement and loss of water: $CHR{:}NO{\cdot}OH + HCl \longrightarrow CHRCl{\cdot}NH(OH){:}O \longrightarrow CHRCl{\cdot}N(OH)_2 \longrightarrow CRCl{:}NOH$. In those cases where the *iso*nitro-compound and the product of its union with the hydrogen haloid exhibit particularly slight stability,

the loss of water may partly precede the rearrangement; a nitroso-compound would then be formed as intermediate product:
$CHR:NO\cdot OH \longrightarrow CHRCl\cdot NH(OH):O \longrightarrow CHRCl\cdot NO \longrightarrow CRCl:NOH$.

Analogous interpretations suggest themselves for the formation of halogen-substituted nitro-products, nitrolic acids and oxides. Further, Nef's reaction does not necessitate the intermediate formation of a ring compound, as it is expressed in all probability by the scheme: $:C:NO\cdot OH + H_2O \longrightarrow :C(OH)\cdot NH(OH):O + H_2O \longrightarrow :C(OH) \cdot NOH + H_2O$. T. H. P.

Nitrosites of the Aliphatic Series. K. V. SIDORENKO (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1585—1604).—The author has devised an improved method for preparing ethylene nitrosite (compare Demjanov, A., 1899, i, 845), a number of reactions of this compound being studied.

When heated in a sealed tube with dilute hydrochloric acid (1 : 1), it yields hydroxylamine, apparently according to the equation:
$$(C_2H_4O_3N_2)_2 + 4H_2O + 4HCl = 2CHO\cdot CO_2H + 4NH_2\cdot OH,HCl.$$
At the ordinary temperature it is dissolved by concentrated sulphuric acid, from which it is precipitated unchanged on dilution. Nitric acid seems to be without action on it in the cold, but in the hot yields oxalic acid.

With aniline in absolute alcoholic solution, it gives a basic compound, and this, with hydrochloric acid, yields a crystalline substance, which is difficult to purify and gives poor results on analysis. Under similar conditions, *p*-nitroaniline acts on it apparently as a catalyst, being obtainable unchanged from the products of the reaction.

With benzylamine it reacts in accordance with the equation:
$(C_2H_4O_3N_2)_2 + NH_2\cdot CH_2Ph = (C_2H_4O_2N_2)_2:N\cdot CH_2Ph + N_2O + H_2O$, the unstable *compound* thus obtained crystallising in long, colourless, silky prisms and exhibiting normal cryoscopic behaviour in benzene.

With dibenzylamine it reacts thus: $(C_2H_4O_3N_2)_2 + 2NH(CH_2Ph)_2 = 2C_2H_4O_2N\cdot N(CH_2Ph)_2 + N_2O + H_2O$, the compound formed crystallising in long prisms, m. p. 74·6—75·2°, and possessing the normal molecular weight in freezing benzene. This compound exhibits feeble basic properties; it exerts a scarcely perceptible alkaline reaction on litmus, and yields no salts, even with strong acids. When reduced with tin and hydrochloric acid, it yields a sparingly soluble hydrochloride, which forms a platinichloride insoluble in alcohol. Accompanying the dibenzylamine derivative is a small quantity of a compound which separates in crystalline granules and possibly represents the result of combination between the amine and the nitrosite after the latter is resolved into two separate molecules.

From these results the conclusion is drawn that ethylene nitrosite has the structure $N_2O_2(CH_2\cdot CH_2\cdot NO_2)_2$, and thus belongs to the class of ψ-nitrosites (compare Wieland, A., 1904, i, 54). T. H. P.

The History of Alcohol. EDMUND O. VON LIPPMANN (*Chem. Zeit.*, 1913, **37**, 1313—1316, 1346—1347, 1358—1361, 1419—1422, 1428—1429. Compare A., 1912, i, 824; ii, 897).—A reply, with

historical quotations, to criticism by Diels of the author's view that alcohol and the process of distillation of readily volatile substances were unknown before the eleventh century. H. W.

Vapour Pressure of Glyceryl Trinitrate at the Ordinary Temperature. D. CHIARAVIGLIO and O. M. CORBINO (*Gazzetta*, 1913, **43**, i, 390—398).—In certain circumstances the rate of cooling of a warm substance situated in a closed space containing a very attenuated gas or vapour is proportional to the concentration of the molecules of the gas or vapour. Applying this method, the authors find that at about 21° the vapour pressure of glyceryl trinitrate is less than 0·0001 mm., so that it is beyond the limits of measurement or even detection. The value for the vapour pressure given by Marshall (*J. Soc. Chem. Ind.*, 1904, **23**, 157; compare P., 1913, **29**, 157) they regard as untrustworthy, because it is based on the assumption that, since the vapour pressures of glyceryl trinitrate and mercury are equal at 70°, they are also equal at the ordinary temperature. R. V. S.

Preparation of Aluminium Ethoxide. CLÉMENT BERGER (*Compt. rend.*, 1913, **157**, 717—718).—Aluminium amalgam acts but slowly on absolute alcohol, but if, prior to the addition of the amalgam, a little sodium is dissolved in the alcohol, then, on warming the mixture under a reflux condenser, a rapid action takes place. When a considerable precipitate has formed, it is filtered off rapidly, and the filtrate evaporated to dryness in a vacuum. The solid residue is *aluminium ethoxide*, $Al(OEt)_3$. It is readily decomposed in the solid state or in solution by water, giving alcohol and aluminium, the presence of small quantities of water stopping its preparation. In the solid state it is decomposed by heat. W. G.

Preparation of Epichlorohydrin. JEAN NIVIÈRE (*Bull. Soc. chim.*, 1913, [iv], **13**, 969—971).—A detailed account of a method already mentioned (compare this vol., i, 697) for the preparation of epichlorohydrin by the interaction of αγ-dichlorohydrin and potassium hydroxide in the presence of small quantities of water. W. G.

Catalytic Preparation and Decomposition of Esters. ALPHONSE MAILHE (*Chem. Zeit.*, 1913, **37**, 777—778, 806—807).—The first paper contains a historical account of the work done on the catalytic preparation and decomposition of esters with particular reference to the more recent experiments of Sabatier and Mailhe on the use of metallic oxides. The second paper is a discussion of the behaviour of esters of aliphatic acids towards metallic oxide catalysts with special reference to formic acid and its esters. H. W.

Preparation of Sparingly Soluble Salts of Aluminium with Formic Acid Alone or with Formic together with Acetic Acid. ALBERT FRIEDLÄNDER (D.R.-P. 263865).—*Aluminium formate*, $Al(OH)(HCO_2)_2$, and *aluminium formoacetate*,

$$HCO_2\cdot Al(C_2H_3O_2)OH,2H_2O,$$

are respectively prepared by heating aluminium hydroxide with anhydrous formic acid or with a mixture of formic and acetic acids; they are of therapeutic value. F. M. G. M.

Ferri- and Chromi-formates. RUDOLF F. WEINLAND and HANS REIHLEN (*Ber.*, 1913, **46**, 3144—3150).—The compounds formed when a ferric salt is treated with sodium formate have been studied. In the deep red solution which results when equivalent quantities are mixed there is present the cation $[Fe_3(H\cdot CO_2)_6]$ of the hexaformato-triferri-base, of which only the monoformate has yet been isolated (Belloni, A., 1909, i, 283; Tower, 1910, ii, 900). By the addition of solid sodium formate to such a solution, the red colour gradually becomes pale, and *trisodium hexaformatoferrate*, $[Fe(H\cdot CO_2)_6]Na_3$, separates in pale green, microscopic, rectangular tablets. Thus, in presence of much sodium formate the anion $[Fe(H\cdot CO_2)_6]$ of hexaformatoferric acid is formed. This recalls the deep green of the trioxalatoferri-anion. By the action of water, the pale green solution or salt becomes red, the complex ions being in equilibrium.

The composition of the red formates, which are formed when ferric salts are mixed with sodium formate, varies, and the formic acid content rises with the concentration of that acid in the solution. It is therefore probable that in these substances there may be present salts of the hexaformatoferri-base with the hexaformatoferric acid. Brick-red, microcrystalline *compounds* which agree with the formulæ $[Fe(H\cdot CO_2)_6][Fe_3(H\cdot CO_2)_6],8H_2O$ and

$$[Fe(H\cdot CO_2)_6]\left[Fe_3\genfrac{}{}{0pt}{}{(H\cdot CO_2)_6}{(OH)_2}\right]_3,14H_2O$$

have been prepared.

Similar phenomena occur in the case of chromium salts. From a solution containing 30 mols. of sodium formate to one of chromium nitrate, *trisodium hexaformatochromate*, $[Cr(H\cdot CO_2)_6]Na_3,4\cdot 5H_2O$, crystallises in greenish-violet rhombohedra, which are only decomposed by ammonia after prolonged boiling. J. C. W.

Two Isomeric Forms of Anhydrous Sodium Acetate. DANIEL VORLÄNDER and OTTO NOLTE (*Ber.*, 1913, **46**, 3199—3212).—An anhydrous form of sodium acetate is obtained on fusing sodium acetate trihydrate below 100°, and it also crystallises from fused sodium acetate. Intermediate hydrates do not exist. This modification is isomeric with that obtained on cooling the amorphous flux prepared by dehydrating above 200°. The new low temperature modification crystallises in the rhombic system and passes into the isomeride at 198°. The change is enantiotropic, the reverse change taking place so slowly that the two forms can exist side by side for months. The decomposition temperature of the trihydrate into water and anhydride is 58·2°.

Both anhydrous forms when crystallised from absolute ethyl or methyl alcohol yield the new rhombic form. This is an excellent condensation agent, absorbing water much more quickly than the ordinary fused form. For such purposes the trihydrate is best dehydrated at 120—160°.

The phenomena of polymorphism are explained on the assumption that within the molecule as a whole there is a difference in the intensity of the energy between the different parts. Further, in consequence of these intramolecular differences there are variable external differences in intensity between similar molecules, so that the molecules become united in different ways. Thus two sodium acetate molecules may be united.

$$\begin{array}{ccc} \mathrm{MeCO{\cdot}ONa} & \mathrm{MeCO{-}ONa} & \mathrm{CH_3{\cdot}CO{\cdot}ONa} \\ \vdots & \vdots\quad\vdots & \ddots\quad\vdots \\ \mathrm{MeCO{\cdot}ONa} & \mathrm{CH_3{\cdot}CO{\cdot}ONa} & \mathrm{NaO{\cdot}CO{\cdot}CH_3.} \end{array}$$

Such differences will explain the different crystalline structure of the polymorphic forms. E. F. A.

The Solidifying- and Melting-points of Mixtures of Stearic and Oleic Acids. ROBERT MELDRUM (*Chem. News*, 1913, **108**, 199—201).—The investigation was undertaken to confirm the degree of accuracy of Dalican's method of determining the solidifying point and the thermometer bulb method of determining the melting point of mixtures of fatty acids.

In the first series of experiments, the solidifying points were taken in a test-tube 7 inches by 1 inch filled three parts full, which was suspended in a glass jar. The mixtures of acids were melted and cooled to within 10° of their solidifying point. The thermometer was inserted and when crystallisation had commenced the whole was very slowly stirred until the thermometer ceased to fall, when the latter was fixed in the centre, 1½ inches from the bottom, and the readings completed. The point at which the thermometer rose and remained stationary was taken as the solidifying point. The method yields very concordant results for any given mixture and, contrary to the general belief, indicates the composition of the mixture more accurately when the solidifying point is low than when it is high.

A second series of experiments was performed in the same apparatus, but without stirring. The results are concordant among themselves, but both rise and solidifying point are lower than indicated by the first method. The rise appears to be rather erratic, and is apparently governed by the amount of matter crystallised per given interval of time. When working with large quantities, it appears to be eliminated.

A series of determinations of m. p. has also been made (1) by covering the thermometer bulb with a thin layer of substance, and suspending it inside a test-tube which is gradually heated in a beaker of water; (2) by the closed capillary tube method; (3) with an open capillary, and (4) with a capillary U-tube both limbs of which are left open. One limb contains a column of solid fat 4 cm. long. The tube is heated in a water-bath, the thermometer being placed between the limbs. The temperature at which both columns of fat are at equal height is taken as the m. p. The conclusion is drawn that the bulb method is the most accurate, the chief difficulty in it lying in obtaining a uniform coating of the fat. In the methods which depend on the displacement of the column of solid (Nos. 3 and 4), movement occurs while the latter is completely molten. H. W.

The Reaction between Acetoacetic Esters and Phenyl Iododichloride. GEORG SACHS (*Monatsh.*, 1913, **34**, 1409—1415).—The application of phenyl iododichloride as a chlorinating agent has been studied in the case of methyl and ethyl acetoacetates. Reaction with the methyl ester commenced at 34—35° and slackened after slightly more than one molecular proportion of phenyl iododichloride had boon added at 60°. On distillation, a constant boiling, inseparable mixture of approximately two molecules of iodobenzene with one molecule of the expected methyl α-chloroacetoacetate, b. p. 84°/30 mm., was obtained. When ethyl acetoacetate was warmed at 60—80° with two molecules of the agent, however, iodobenzene, b. p. 79°/23 mm., and ethyl α-dichloroacetoacetate, b. p. 99°/21 mm., 207°/753 mm., were obtained. J. C. W.

Optically Active Dimethylsuccinic Acid. ALFRED WERNER and M. BASYRIN (*Ber.*, 1913, **46**, 3229—3232).—It is shown that dimethylsuccinic acid may be resolved by means of optically active triethylenediaminecobaltic bromide. The modification of dimethylsuccinic acid, m. p. 195°, could not be resolved, and accordingly it represents the *meso*-form. The form m. p. 127° gives rise to d-*triethylenediaminecobaltic bromide* l-*dimethylsuccinate*, which is sparingly soluble, whereas the mother liquors contain the corresponding d-*dimethylsuccinate*. The optically active dimethylsuccinic acids have m. p. 135° and $[\alpha]_D$ +7·8° and −8·0.° E. F. A.

Ketonic Decomposition of β-Lactones and its Application to the Synthesis of Ketens. ERWIN OTT (*Annalen*, 1913, 401, 159—177).—Somewhat similar to the behaviour of dialkylmalonic anhydrides by heating, whereby dialkylketens are formed (Staudinger and Ott, A., 1908, i, 602), is the behaviour of derivatives of Meldrum's β-lactone of β-hydroxy*iso*propylmalonic acid (T., 1908, **93**, 601). In these also, by heating, the 4-ring is broken and acetone and ketens are obtained. The β-lactone of β-hydroxy*iso*propylmalonic acid decomposes by heating into carbon dioxide, carbon suboxide, acetone, and acetic acid.

The *β-lactone* of *β-hydroxy-α-methyl*iso*propylmalonic acid*,

$$\begin{array}{l} O{-}CMe_2 \\ |\qquad\ | \\ CO{\cdot}CMe{\cdot}CO_2H \end{array}$$

decomp. 110—113°, colourless leaflets, is obtained by treating methylmalonic acid with acetic anhydride and a little concentrated sulphuric acid, and keeping the product for many days with the calculated amount of acetone. The lactonic acid decomposes by heating into carbon dioxide, acetone, and viscous substances. It cannot be esterified directly, but the *methyl* ester, $C_8H_{12}O_4$, m. p. 59·5°, b. p. 71°/0·1 mm., is obtained, together with the β-lactones of β-hydroxy*iso*propylmalonic acid and of β-hydroxy-α-methyl*iso*propylmalonic acid, in a remarkable reaction between methyl iodide and the β-lactone of silver β-hydroxy*iso*propylmalonate. The methyl ester, which is remarkably stable and distils at 213°/723·4 mm., with only slight decomposition, yields, by heating in a current of hydrogen, carbon dioxide, acetone, and about 50% of dimethylketen.

The β-*lactone* of *a-bromo-β-hydroxy*iso*propylmalonic acid*,

$$\begin{array}{l} \mathrm{O}\text{---}\mathrm{CMe_2} \\ \vert \quad\;\; \vert \\ \mathrm{CO\cdot CBr\cdot CO_2H} \end{array}$$

decomp. 87—92°, colourless needles, is prepared by exactly neutralising the β-lactone of β-hydroxy*iso*propylmalonic acid with 2*N*-sodium hydroxide in the cold and treating the solution slowly with the calculated amount of bromine. At 130° the brominated lactonic acid decomposes into acetone, carbon dioxide, and hydrogen bromide.

The *methyl* ester, $C_7H_9O_4Br$, m. p. 87°, colourless prisms, prepared from the silver salt and methyl iodide in benzene, is decomposed by slow distillation at 95° over a faintly glowing platinum spiral in a vacuum, whereby carbon dioxide, acetone, and *bromomethylketen*, CBrMe:CO, are obtained. Bromomethylketen is being fully examined; it polymerises with great readiness to a faintly yellow, resinous *substance*, $(C_3H_3OBr)_5$, m. p. 60—70°, and differs from all other ketens in not reacting with aniline.

Malonic acid and acetic anhydride in the presence of a little concentrated sulphuric acid yield, after removal of the excess of the anhydride and the acetic acid at 30—40°/1—2 mm., an extremely hygroscopic oil which is presumably the mixed malonic acetic anhydride, since it contains for each molecule of malonic acid, one acetyl group which cannot be removed without decomposition. The substance yields carbon suboxide by warming on the water-bath, and reacts with acetone to give an 87% yield of the β-lactone of β-hydroxy*iso*propylmalonic acid. Dimethylmalonic anhydride is obtained in 96% yield by treating dimethylmalonic acid with acetic anhydride and a little concentrated sulphuric acid, and removing by-products at 40°/1—2 mm., the operations being once repeated on the product. *Diethylmalonic anhydride*, prepared in a similar manner, is a liquid. C. S.

Synthesis of Formaldehyde from Carbon Dioxide and Water by Inorganic Colloids acting as Transformers of Light Energy. BENJAMIN MOORE and T. ARTHUR WEBSTER (*Proc. Roy. Soc.*, 1913, [*B*], **87**, 163—176).—The experiments of Bach, Euler, Usher, and Priestley (compare A., 1906, ii, 299, 881) have been confirmed and extended to show that formaldehyde is synthesised from carbon dioxide by means of inorganic colloidal uranic and ferric hydroxides in very dilute solution. The colloids act as catalysts for light energy, positive results being obtained only in strong, direct sunlight and in a "uviol" mercury arc. Under similar conditions, crystalloid uranium nitrate does not cause synthesis. The uranium catalyst is more powerful than the ferric catalyst. It is claimed that such a process occurring in nature forms the first step in the origin of life.

E. F. A.

Condensation of Aldol with Formaldehyde. V. P. KRAVEC (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1451—1453).—With the object of obtaining derivatives of pentaerythritol, from which the hydrocarbon, C_5H_8, regarded by Gustavson (A., 1896, i, 669) as vinyltrimethylene, has been obtained (compare Zelinski, this vol., i, 251), the author has investigated the condensation of aldol with formaldehyde under the

conditions laid down by Tollens and Wigand (A., 1892, 127): this reaction may be expected to give methylpentaerythritol.

Aldol may be readily prepared in good yield (30 grams) by a method devised by Zelinski and Volkonski, but not yet published. It consists in mixing acetaldehyde (100 grams), dissolved in an equal weight of water, with freshly precipitated, alkali-free lead hydroxide (30 grams), at a temperature not exceeding 5°, the mixture being left at the ordinary temperature for two hours and then gradually heated on the water-bath at 25°, 30°, and 35° during eighteen hours.

In presence of lead hydroxide, aldol and formaldehyde give pentaerythritol, so that resolution of the aldol molecule into 2 mols. of acetaldehyde precedes condensation with formaldehyde. The action of lead hydroxide on aldol is hence a typical, reversible reaction (compare de Bruyn and Alberda van Ekenstein, A., 1899, i, 851; Löb, A., 1909, i, 767; Löb and Pulvermacher, A., 1910, i, 95).

Pentaerythritol is also obtained from aldol and formaldehyde in presence of calcium hydroxide, but the latter is not able to effect the condensation of acetaldehyde to aldol. T. H. P.

Mechanism of Oxidative Changes. HEINRICH WIELAND (*Ber.*, 1913, 46, 3327—3342).—The catalytic action of palladium or platinum is not due to the activation of molecular oxygen with intermediate formation of peroxide, but it is attributed to the activation of hydrogen This theory is extended to biological oxidations, and it is shown that certain of these can take place in presence of palladium black and in the complete absence of oxygen, provided that the accumulated hydrogen is removed by the presence of other substances with an affinity for hydrogen such as *p*-benzoquinone or methylene-blue.

Dextrose can be dehydrogenated by shaking with palladium black at 40° in an atmosphere of nitrogen, carbon dioxide being formed from the beginning of the reaction as well as hydrogen. The change is accelerated on the addition of *p*-benzoquinone, which is converted into quinhydrone or of methylene-blue, which is decolorised. In presence of oxygen which forms water with the liberated hydrogen, the change is still more rapid. Gluconic acid is even more quickly dehydrogenated.

Lactic acid yields pyruvic acid under similar conditions. Phenol, *m*-cresol, guaiacol, pyrogallol and aniline can be dehydrogenated in the absence of oxygen. Tyrosine and uric acid are resistant, but in both these cases the action of the oxydase is known to be combined with that of a hydrolysing enzyme.

Alcohol in presence of methylene-blue or of *p*-benzoquinone is converted into acetic acid by an acetone preparation of acetic acid bacteria, all oxygen being excluded. Acetaldehyde behaves similarly, whereas methyl alcohol or formaldehyde are converted into formic acid. Dextrose is dehydrogenated by the acetic acid ferment in presence of methylene-blue, carbon dioxide being formed.

The reducing enzymes, for example, Schardinger's reductase, act in the same manner. Salicylaldehyde is converted into salicylic acid by the milk enzyme either in presence of oxygen or in presence of methylene-blue in the absence of oxygen. E. F. A.

Biochemical Synthesis of a Sugar of the Hexobiose Group, Gentiobiose. ÉMILE BOURQUELOT, HENRI HÉRISSEY, and J. COIRRE (*Compt. rend.*, 1913, **157**, 732—734; *J. Pharm. Chim.*, 1913, [vii], **8**, 441—449).—The authors have prepared and isolated gentiobiose in a pure state by the action of emulsin, from almonds, on a concentrated solution of dextrose at 15—20° for one month. The excess of dextrose was removed by fermenting it with top yeast, after destroying the emulsin by heat and diluting the solution. The fermented liquid was neutralised with calcium carbonate, filtered and evaporated to dryness under reduced pressure. The dry residue was extracted with 95% alcohol, from which extracts two crops of crystals were obtained, the first containing mineral matter, and the second being pure gentiobiose as shown by its physical and chemical properties. W. G.

Peculiarity in the Solubility Curve of Sugar in Water. PH. ORTH (*Bull. Assoc. chim. Sucr. Dist.*, 1913, **31**, 94—103).—A theoretical paper. It is shown that the equation $S = 28162/(157·97 - t)$ gives the solubility of sucrose in water at a temperature t. The coefficient of supersaturation C_1 is obtained by the expression $C_1 = S(157·97 - t_1)/28162$, in which S is the solubility at a temperature t and t_1, the lower temperature to which the solution is cooled without crystallisation. The constant 157·97 is shown to represent the temperature at which the solubility of sucrose in water becomes infinitely large, that is, the temperature at which sucrose and water are miscible in all proportions. A number of other empirical equations are given dealing with the freezing-point constant and the specific heat of aqueous solutions of sucrose, and also with the heat of solution.

J. F. S.

The Nitration of Cellulose, and the Decomposition of Nitrocellulose by Acids and Alkalis. G. MEISSNER (*Zeitsch. ges. Schiess. Sprengstoffwesen*, 1913, **8**, 252—254, 269—271).—An account of numerous experiments on the yields, stability, and variations in the products obtained by nitrating cellulose under different conditions, together with an account of the decomposition of these compounds by acids and alkalis. F. M. G. M.

Unstable Products in the Nitration of Cellulose. ERNST BERL and MAX DELPY (*Zeitsch. ges. Schiess. Sprengstoffwesen*, 1913, **8**, 129).—When water is removed from nitrocellulose by systematic treatment with alcohol, it gives rise to a brown powder, decomp. 162°, soluble in concentrated sulphuric acid; this when extracted with ether furnishes two *compounds*: (1) a yellowish-brown powder, decomposing at 174°, containing about 10% of nitrogen, and converted by concentrated alkalis into a compound soluble in water; and (2) a violet powder containing 9·45% of nitrogen and decomposing at 157°.

F. M. G. M.

Fatty Acid Esters of Hydrocellulose and their Hydrolysis. ALBRECHT STEIN (*Zeitsch. angew. Chem.*, 1913, **26**, 673—677).—Triacyl derivatives of hydrocellulose are prepared without difficulty by

acting on hydrocellulose with the anhydride of a fatty acid in the presence of concentrated sulphuric acid. The properties of the hydrocellulose esters of the homologues of acetic acid are similar to those of acetyl cellulose.

In order to obtain information as to the manner in which the catalyst acts in the esterification of hydrocellulose, the action of an acid anhydride on hydrocellulose in the presence of chloroacetic acid or trichloroacetic acid has been studied. It is found that the use of these catalysts leads to the production of an ester containing chlorine, in some cases to the extent of 2·8%. W. H. G.

The Preparation of Triethylamine. JITENDRA NATH RAKSHIT (*J. Amer. Chem. Soc.*, 1913, **35**, 1781—1783).—If 75 c.c. of ethyl bromide and 50 c.c. of ammonia solution (D 0·88) are heated together in a closed 750 c.c. flask in the steam-oven for three hours, subsequent distillation with sodium hydroxide solution into dilute hydrochloric acid gives a mixture of ammonium chloride and ethylamine hydrochloride which are most easily separated by filtering the latter in a molten condition from the solid ammonium chloride.

The ethylamine from 62 grams of the hydrochloride is then mixed with 44 c.c. of ethyl bromide and again heated in a closed flask for three hours in the steam-oven. After cooling, the liquid is decanted from the separated crystalline solid and is then evaporated with dilute hydrochloric acid, when the residue (approximately 19 grams) consists of pure triethylamine hydrochloride. D. F. T.

Resolution of α-Alanine into its Optical Antipodes by means of Active Acids. II. AMEDEO COLOMBANO and GIUSEPPE SANNA (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 292—298. Compare this vol., i, 1208).—In alcoholic solution, the ethyl ester of alanine and *d*-camphorsulphonic acid yield the *salt* of the *inactive* ester,

$$CO_2Et\cdot CHMe\cdot NH_2,C_{10}H_{15}O\cdot SO_3H,\tfrac{1}{2}H_2O,$$

m. p. 95—100°, $[\alpha]_D$ +11·49°. When water is used as solvent, crystalline fractions are obtained of gradually increasing melting point and specific rotation, but separation of the *d*- and *l*-alanines in this way is not easy

Such resolution is, however, readily effected by means of *d*-bromocamphorsulphonic acid, mixing of the ammonium salt of this acid with alanine ester hydrochloride in aqueous solution resulting in the separation of *ethyl* d-*alanine* d-*bromocamphorsulphonate*,

$$CO_2Et\cdot CHMe\cdot NH_2,C_{10}H_{14}OBr\cdot SO_3H,1H_2O,$$

m. p. 145° or 192° (anhydrous), $[\alpha]_D^{25}$ +67·54° (hydrate), which corresponds with the dextro ester and with *l*-alanine. Isolation of ethyl *l*-alanine *d*-bromocamphorsulphonate from the mother liquor is troublesome and gives only a small yield; possibly this ester could be more readily obtained by the use of *l*-bromocamphorsulphonic acid. T. H. P.

Tetra-aminoadipic Acid and αδ-Dihydroxy-βγ-diaminoadipic Acid. WILHELM TRAUBE and ARTHUR LAZAR (*Ber.*, 1913, **46**, 3438—3450. Compare A., 1903, i, 76).—An account of the replacement of the bromine atoms in the monolactam of αδ-dibromo-βγ-di-

aminobutane-$\alpha\alpha\delta\delta$-tetracarboxylic acid (I) and the dilactam of $\alpha\delta$-dibromo-$\beta\gamma$-diaminoadipic acid (II) by the hydroxyl amino-, and dimethylamino-groups :

$$\text{(I.)}\quad CBr(CO_2H)_2\cdot CH<\begin{matrix}CH(NH_2)\\ NH\text{—}CO\end{matrix}>CBr\cdot CO_2H$$

$$\text{(II.)}\quad CO<\begin{matrix}CHBr\cdot CH\text{—}NH\\ NH\text{—}CH\cdot CHBr\end{matrix}>CO.$$

When heated at 105° with alcoholic ammonia, the dilactam of dibromodiaminoadipic acid is converted into the *dilactam* of *$\alpha\beta\gamma\delta$-tetra-aminoadipic acid*, $CO<\begin{matrix}NH\text{———}CH\cdot CH(NH_2)\\ CH(NH_2)\cdot CH\text{———}NH\end{matrix}>CO$, which crystallises in stellar aggregates of short, stout needles, and forms a sparingly soluble *sulphate*, B,H_2SO_4 (solubility in water at 100° = 0·177 : 100), a *nitrate* (leaflets), *platinichloride* (hexagonal pyramids or rhombohedra), *hydrochloride* (colourless, prismatic needles), and *picrate* (fern-like aggregates).

The hydrochloride reacts with potassium cyanate in hot aqueous solution, yielding the *dilactam* of *$\beta\gamma$-diamino-$\alpha\delta$-dicarbamidoadipic acid*, $C_8H_{12}O_4N_8$, which crystallises with water (1 mol.) in colourless needles.

Attempts to prepare tetra-aminoadipic acid by acidifying solutions of the dilactam in aqueous alkalis were unsuccessful, the original dilactam being precipitated unchanged.

The *dilactam* of *α-bromo-$\beta\gamma\delta$-triamino-α(or δ)carboxyadipic* [*α-bromo-$\beta\gamma\delta$-triaminobutane-$\alpha\gamma\gamma$*(or *$\alpha\alpha\gamma$*)*-tricarboxylic*] *acid*, $C_7H_8O_4N_3Br$, obtained in the form of its *ammonium* salt by the action of alcoholic ammonia at 80—90° on the monolactam of $\alpha\delta$-dibromo-$\beta\gamma$-diaminobutane-$\alpha\alpha\delta\delta$-tetracarboxylic acid, crystallises with water ($1\frac{1}{2}$ mol.) in needles (decomp. 280°) and yields salts with both bases and acids; the *silver* salt (slender, colourless needles), *barium* salt, and *hydrobromide* (prisms) are described. The position of the free carboxyl group has not yet been determined. When kept in contact with an excess of aqueous dimethylamine (45%) for four or five days at the ordinary temperature, the dilactam of $\alpha\delta$-dibromo-$\beta\gamma$-diaminoadipic acid is converted into the *dilactam* of *$\beta\gamma$-diamino-$\alpha\delta$-tetramethyldiaminoadipic acid* (III), which is separated from the accompaning *3 : 4-diaminotetrahydrofuran-2 : 5-dicarboxylic acid* (IV) by taking advantage of the sparing solubility of the latter compound in water.

$$\text{(III.)}\quad CO<\begin{matrix}NH\text{———}CH\cdot CH(NMe_2)_2\\ CH(NMe_2)_2\cdot CH\text{———}NH\end{matrix}>CO.$$

$$\text{(IV.)}\quad \begin{matrix}CO_2H\cdot CH\cdot O\cdot CH\cdot CO_2H\\ NH_2\cdot CH\text{—}CH\cdot NH_2\end{matrix}.$$

The furan compound crystallises in ill-defined tetragonal prisms which become yellow at 210°, and have m. p. 230° (decomp.). It forms with mineral acids very hygroscopic salts, of which the *nitrate* (decomp. 180°) is described. On treatment with fuming nitric acid, it yields *2-nitro-3 : 4-diaminofuran-5-carboxylic acid*, $C_5H_5O_5N_3$, crystallising in stellar aggregates of slender needles (decomp. above 300°). The dilactam, III, separates with $2H_2O$ in

well developed rhombic crystals, which darken at 243° and have m. p. 252° (decomp.). It forms a *hydrochloride*, $B,2HCl$, long, slender needles; a *picrate*, hexagonal leaflets; *platinichloride*, rectangular plates; *sulphate*, rhombic prisms, and an *oxalate*, prismatic needles.

The monolactam of αδ-dibromo-βγ-diaminobutane-ααδδ-tetracarboxylic acid reacts with silver nitrate in aqueous solution, yielding the *silver* salt, $C_8H_6O_7N_2Br_2Ag_2$, which is converted by boiling with water into the *monolactam* of *βγ-diamino-αδ-dihydroxybutane-ααδ-tetracarboxylic acid*, $OH{\cdot}C(CO_2H)_2{\cdot}CH{<}{\genfrac{}{}{0pt}{}{CH(NH_2)}{NH{-}{-}CO}}{>}C(OH){\cdot}CO_2H$. The latter compound could not be obtained crystalline, and, therefore, was isolated in the form of its *silver* salt, $C_8H_9O_9N_2Ag$.

When heated either alone at 180° or in aqueous solution, it loses carbon dioxide and water, yielding the *dilactam* of *βγ-diamino-αδ-dihydroxyadipic acid*, $CO{<}{\genfrac{}{}{0pt}{}{CH(OH){\cdot}CH{-}{-}{-}{-}NH}{NH{-}{-}{-}{-}CH{\cdot}CH(OH)}}{>}CO$, which crystallises in tetragonal prisms capped with pyramids.

Attempts to prepare tetrahydroxyadipic acid from the dilactams of tetra-aminoadipic and αδ-dihydroxy-βγ-diaminoadipic acids proved unsuccessful, the amino-groups in these compounds being stable towards the action of nitrous acid. F. B.

Preparation of Acetamide. E. F. Hitch and H. N. Gilbert (*J. Amer. Chem. Soc.*, 1913, **35**, 1780—1781).—Acetamide is conveniently prepared by heating a mixture of 42 grams of ammonium carbonate and 125 grams of acetic acid (compare Rosanoff, Gulick, and Larkin, A., 1911, i, 529) in a 250 c.c. round-bottomed flask in an air-bath. The flask is fitted with a Vigreux fractionating column carrying a thermometer and attached to a condenser. The mixture is boiled at such a rate that 20 to 30 drops distil per minute, and when the thermometer registers 223° the residue in the flask is almost pure acetamide.

The yield is 85—90% calculated on the ammonium carbonate, and the time required is four hours. D. F. T.

Synthesis of Amido-oxalylbiuret. Johan Th. Bornwater (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 198—200).—In a previous paper (A., 1911, i, 617) the author has shown that finely-powdered carbamide reacts with an ethereal solution of oxalyl chloride, yielding parabanic acid and, apparently, oxalyldiureide,

$$C_2O_2(NH{\cdot}CO{\cdot}NH_2)_2,$$

which is quite different from Grimaux's compound (A., 1880, 105) obtained by fusion of a mixture of carbamide and parabanic acid. Subsequently, the subject has been re-investigated by Biltz and Topp (this vol., i, 600, 602), who are led to the conclusion that the two substances are probably identical, although certain differences remain unexplained. The author points out that Grimaux's compound has been incorrectly described as oxalyldiureide in the German literature, since Grimaux calls it, "amide d'un acide oxalylbiurétique." He has further effected the synthesis of the latter compound.

[illegible]oxyethoxalylcarbamide, $CO_2Et\cdot NH\cdot CO\cdot NH\cdot CO\cdot CO_2Et$, needles, m. p. 152°, is obtained in 10% yield when ethyl oxamate and ethyl urethane are heated in dry benzene. When a solution of this substance in absolute alcohol is treated with dry, gaseous ammonia, amido-oxalylbiuret, $NH_2\cdot CO\cdot CO\cdot NH\cdot CO\cdot NH\cdot CO\cdot NH_2$, is precipitated, which is identical with Grimaux's compound.

In effecting the biuret reaction, the author points out the desirability of first adding the highly diluted copper sulphate solution, and, subsequently, a solution containing at most 15% of potassium hydroxide. When the reagents are added in the reverse order and more concentrated solutions of potassium hydroxide are employed (compare Biltz and Topp, *loc. cit.*), there is a possibility that the substance is already undergoing partial decomposition before the copper sulphate is added.

The substance, $C_4H_5O_3N_3$, m. p. 272—273° (decomp.), obtained by the action of fuming hydriodic acid (D 1·96) on Grimaux's compound, is possibly uramil, the formation of which is explicable on the author's formulation of Grimaux's compound. H. W.

Simultaneous Reduction and Oxidation. I. Dichloropyruvic Acid, Nitrile and Ester from Trichlorolactic Acid, Nitrile and Ester. ARTHUR KÖTZ and K. OTTO (*J. pr. Chem.*, 1913, [ii], 88, 531—552. Compare Wallach, this Journ., 1875, 351; A., 1878, 285, 288; Pinner, this Journ., 1877, ii, 584; A., 1884, 1298).—With the object of throwing further light on the mechanism of the transformation of chloral into dichloroacetic acid under the influence of aqueous potassium cyanide, the authors have undertaken a systematic examination of similar cases of simultaneous reduction and oxidation occurring in compounds of the type $CCl_3\cdot CH(OH)\cdot R$, the present paper dealing particularly with the transformation of $\beta\beta\beta$-trichlorolactic acid, and its nitrile and ester into the corresponding derivatives of dichloropyruvic acid.

They consider that the first stage in the reaction between chloral and potassium cyanide consists in the formation of $\beta\beta\beta$-trichlorolactonitrile (I), and that this loses hydrogen chloride, yielding the compounds (II) or (III), which are at once transformed into dichloropyruvonitrile (IV), the latter compound then undergoing hydrolysis to dichloroacetic and hydrocyanic acids:

$$(I)\ CCl_3\cdot CH(OH)\cdot CN \longrightarrow (II)\ CCl_2{:}C(OH)\cdot CN, \text{ or}$$

$$(III)\ \overbrace{CCl_2\cdot CH}^{O}\cdot CN \longrightarrow (IV)\ CHCl_2\cdot CO\cdot CN \longrightarrow CHCl_2\cdot CO\cdot OH + HCN.$$

The following evidence is given in support of the view that $\beta\beta\beta$-trichlorolactonitrile is intermediately formed in the reaction: (1) Although potassium cyanide is hydrolysed to potassium hydroxide and hydrogen cyanide, the action of potassium cyanide on chloral does not give rise to chloroform, and therefore the chloral cannot be present as such in the mixture. (2) $\beta\beta\beta$-Trichlorolactonitrile, on treatment with potassium hydroxide, gives rise to potassium dichloroacetate, no chloroform being produced in the reaction.

$\beta\beta\beta$-Trichlorolactonitrile thus differs from chloral in not undergoing hydrolysis with the formation of chloroform. This difference is referred by the authors to the reactivating influence of the cyanogen group on the hydrogen atom directly attached to the central carbon of the nitrile; on account of this mobility of the hydrogen atom, the molecule readily loses hydrogen chloride, whilst at the same time the ability to yield chloroform by hydrolysis disappears.

A similar differance is shown by $\beta\beta\beta$-trichloroethyl alcohol, ethyl $\beta\beta\beta$-trichlorolactate, and other compounds of the type

$$CCl_3\cdot CH(OH)\cdot R.$$

On treatment with triethylamine, ethyl $\beta\beta\beta$-trichlorolactate and $\beta\beta\beta$-trichlorolactonitrile lose hydrogen chloride, yielding ethyl dichloropyruvate and dichloropyruvonitrile. The last-mentioned compound reacts with water and alcohol, yielding dichloroacetic acid and ethyl dichloroacetate.

The formation of dichloroacetamide, dichloroacetanilide, and ethyl dichloroacetate by the action of ammonia, aniline and alcohol on $\beta\beta\beta$-trichlorolactonitrile (Pinner and Wallach, *loc. cit.*) is considered by the authors to furnish additional support to their view that dichloropyruvonitrile is formed as an intermediate product in the action of potassium cyanide on chloral.

When heated with water or triethylamine, trichlorolactic acid decomposes, thus: $CCl_3\cdot CH(OH)\cdot CO_2H \longrightarrow HCl + CHCl_2\cdot CO\cdot CO_2H \longrightarrow CO_2 + CHCl_2\cdot CHO$.

The readiness with which this decomposition takes place affords an explanation of the fact that the interaction of trichlorolactic acid and ammonia, hydroxylamine, phenylhydrazine, or carbamide gives rise to derivatives of glyoxal or dichloroacetaldehyde.

Dichloropyruvonitrile is obtained (1) by the interaction of molecular proportions of trichlorolactonitrile and triethylamine in ethereal solution at the ordinary temperature, and (2) by heating dichloroacetyl chloride with silver cyanide. It forms a colourless liquid, b. p. 111—113°/12 mm.

$\beta\beta$-Dichloro-α-benzyliminopropiobenzylamide,

$$CHCl_2\cdot C(:N\cdot C_7H_7)\cdot CO\cdot NH\cdot C_7H_7,$$

prepared by heating ethyl trichlorolactate with benzylamine (3 mols.) in ethereal solution, crystallises with water (1 mol.) and has m. p. 161 (not sharp). It may also be obtained by heating ethyl dichloropyruvate with benzylamine (2 mols.) in ethereal solution. When prepared by the second method, it crystallises with $2H_2O$ in lustrous, white leaflets, m. p. 220—221°, or slender needles, m. p. 104 and 150°.

Ethyl dichloropyruvate, prepared by heating ethyl trichlorolactate and triethylamine in alcoholic solution, is a colourless liquid, b. p. 115°/12 mm. It rapidly takes up water on exposure to air, and then has the composition $C_5H_6O_3Cl_2,2H_2O$.

Dichloropyruvic acid, $C_3H_2O_3Cl_2,H_2O$, obtained by hydrolysing the ester with hydrochloric acid, separates from a mixture of ether and light petroleum in white crystals, m. p. 119°, b. p. 215—220°, and after distillation has m. p. 110°. When boiled with water, it is converted into dichloroacetaldehyde.

F. B.

Nitrogen Carbides. Hermann Pauly and Ernst Waltzinger (*Ber.*, 1913, **46**, 3129—3140).—It has already been shown (A., 1910, i, 630) that tetraiodoglyoxaline decomposes on heating to form the compounds C_3N_2I and then C_3N_2, the reaction recalling the formation of paracyanogen from cyanuric iodide (Klason, 1886, 1001). The fact that the decomposition takes place at a temperature which, according to experience, is not inimicable to the glyoxaline ring, suggests that the compounds formed still have ring structure, since a partial loss of nitrogen might be expected to ensue if the ring were opened. In order to test this point, and also to learn whether the preliminary decomposition into a monoiodo-compound was general, tri-iodo-5- and 2-methyl-glyoxalines and tetraiodopyrrole (iodole) have also been heated. In these cases, however, the compounds melt and enclose some of the liberated iodine, so that the formation of intermediate compounds was masked, and, in addition, the presence of hydrogen was disturbing and led to the production of a little ammonium iodide.

All the compounds obtained, C_3N_2, C_3N_2Me and C_4NH, are amorphous, charcoal-like products, and have, in common with paracyanogen, the following properties: they yield cyanogen on heating to redness in an indifferent atmosphere; they give up all their nitrogen as ammonia when heated with soda-lime; they dissolve in molten alkalis, forming ammonia, cyanides and carbonates. Animal charcoal has some of these properties, but does not dissolve in molten alkali. It may consist in part of such nitrogen carbides.

Quantitative studies on the decomposition of tetraiodoglyoxaline were carried out in a glass tube which was slightly bent downwards, so that it dipped below the surface of a metal bath. One end of the tube was attached to a U-tube and a flask containing potassium iodide solution for the absorption of iodine. The iodine was swept out by a stream of carbon dioxide. Since the tetraiodoglyoxaline cannot be purified by recrystallisation, it was analysed before use. It was found that, however carefully prepared, it contained about 1% of a by-product which could be removed by volatilisation at 105° in vacuum. The carbides obtained, readily absorbed gases and moisture, so that all analytical processes were carried out with the greatest expedition.

The formation of the soot-like, sepia-coloured *iodo-nitrogen carbide*, $(C_3N_2I)_x$, takes place at 180°. The substance forms a brown solution in nitric acid, iodine being liberated. The *carbide*, $(C_3N_2)_x$ is best obtained by heating tetraiodoglyoxaline, first at 180° and then at 420°. When heated at 800—900° in a current of carbon dioxide, cyanogen and a little carbon monoxide were formed, but in an atmosphere of nitrogen, the formation of cyanogen was quantitative. J. C. W.

Iron Salts which Combine with Carbon Monoxide. II. The Action of Amines on Sodium Nitroprusside. Wilhelm Manchot and Pierre Woringer (*Ber.*, 1913, **46**, 3514—3521).—It has been shown previously (A., 1912, i, 955) that the action of ammonia on sodium nitroprusside is expressed by the equation:

$$Na_2[Fe(CN)_5NO] + 3NH_3 + H_2O =$$
$$Na_2(NH_4)[Fe(CN)_5NH_3] + NH_4\cdot NO_2.$$

It has now been found possible to replace the NO-group by alkyl-amines instead of ammonia, and the compounds thus formed give similar reactions to the ammonia compound, and also possess the property of combining with carbon monoxide and oxygen. Methyl-amine, dimethylamine, trimethylamine, and ethylenediamine react very readily, but aromatic amines, such as aniline, toluidine, etc., have no action on sodium nitroprusside.

Trisodium ferropentacyanomethylamine, $Na_3[Fe(CN)_5,NH_2Me]$, was obtained in the form of yellow crystals from sodium nitroprusside and methylamine in aqueous methyl-alcoholic solution, dilution with the alcohol being necessary to moderate the reaction. The reaction mixture also contained sodium acetate, to prevent the formation of a disodium methylamine salt.

The *disodium ethylenediamineferropentacyanoethylenediamine*,

$$Na_2[Fe(CN)_5],C_2H_4(NH_2)_2,$$

was not obtained pure, although the product was well crystallised, and appeared homogeneous under the microscope. The addition of sodium acetate to the reaction mixture did not give a trisodium salt.

Although sodium nitroprusside does not react with pyridine, the salt *trisodium ferropentacyanopyridine*, $Na_3[Fe(CN)_5,C_5H_5N]$, can be obtained by the action of pyridine on an aqueous-methyl alcoholic solution of trisodium ammonium ferropentacyanoammine. It crystallises as a felted mass of long, yellow needles, and possesses properties similar to those of the alkylamine compounds.

Experiments to prepare the ferric compounds corresponding with the ferropentacyanocarbon monoxide salts have not hitherto been successful. T. S. P.

Action of Organomagnesium Compounds on Ethyl Diazoacetate. Ernst Zerner (*Monatsh.*, 1913, **34**, 1609—1630).—By means of the reaction between organomagnesium compounds and ethyl diazoacetate or diazomethane, the author hoped to be able to throw some light on the constitution of aliphatic diazo-compounds. No direct proof of the ring or open-chain structure could be obtained, but the results offer more support to the latter view than to the former. The author critises the Angeli-Thiele formula, R:N:N, however, and proposes instead the type R:N·N, making the active nitrogen atom univalent.

Although Thiele has suggested that certain reactions of nitrous oxide agree with the constitution O:N:N, it was found that the gas has no action whatever on magnesium methyl iodide. When ethyl diazotate was added to magnesium methyl iodide at 0°, however, a vigorous reaction occurred, and a crystalline solid and an oil were obtained. The former was most probably the *methylhydrazone of ethyl glyoxylate*, $CO_2Et·CH:N·NHMe$. It formed long, colourless needles, m. p. 91—92°, responded to Molisch's thymol reaction and Tollens's naphtharesorcinol test, and reduced ammoniacal silver and Fehling's solutions. It was hydrolysed by warm dilute sulphuric acid, and methylhydrazine sulphate and ethyl glyoxalate were obtained. An *acetyl* derivative, $C_7H_{12}O_3N_2$, was also prepared, in freely soluble white needles, m. p. 67—69°. The oily product also gave methyl-

hydrazine on hydrolysis. It was probably impure methylhydrazone of hydroxyisobutaldehyde, $OH\cdot CMe_2\cdot CH\colon N\cdot NHMe$. The crystalline compound might also have been ethyl *N*-methylhydraziacetate, $CO_2Et\cdot CH{<}\overset{NH}{\underset{NMe}{|}}$, but this would assume that the diazo-compound reacts differently from the fatty azoimides, which, under the influence of organomagnesium haloids, yield fatty diazoamino-compounds, as Dimroth has shown.

To elucidate this point the action of ethyl diazoacetate on magnesium phenyl bromide was investigated, since it was expected that either the known phenylhydrazone of ethyl glyoxylate or an isomeride would be obtained. However, the only crystalline product was one in which the ester group had also been attacked. It was most probably the *phenylhydrazone* of *hydroxydiphenylacetaldehyde*, $OH\cdot CPh_2\cdot CH\colon N\cdot NHPh$. It crystallised in large, rectangular plates, m. p. 132°, and yielded a red, crystalline *product*, $C_{20}H_{16}N_2$, m. p. 69—70°, on boiling with dilute sulphuric acid, water being eliminated. The red compound gave intense, red solutions in concentrated mineral acids. On evaporating the solution in hydrochloric acid in a desiccator over lime, a snow-white, additive *product*, $C_{20}H_{17}N_2Cl$, was obtained. This was very sparingly soluble in water, but gave a turbidity with silver nitrate. It was freely soluble in organic media, and exhibited a fine blue fluorescence in alcohol. Here again the crystalline product might have been the hydrazi-compound, $OH\cdot CPh_2\cdot CH{<}\overset{NPh}{\underset{NH}{|}}$, but this did not give a condensation product with any chromophoric groups.

Magnesium ethyl iodide and ethyl diazoacetate were also brought together, and ethylhydrazine sulphate was obtained by hydrolysing the unpleasant smelling, brown syrup which resulted.

When diazomethane was distilled into magnesium benzyl chloride, an oily product which contained crystals of either the benzylhydrazone of formaldehyde, or benzylhydrazimethylene, was obtained. The *compound*, $C_8H_{10}N_2$, formed stable, white plates, m. p. 124°, whereas a crystalline product obtained by mixing 40% formaldehyde and benzylhydrazine was very unstable. J. C. W.

Organic Silicon Compounds which Liberate Hydrogen from Silicon Hexachloride and Magnesium Methyl Bromide or Iodide. GEOFFREY MARTIN (*Ber.*, 1913, **46**, 3289—3295. Compare this vol., i, 961).—By the action of magnesium methyl bromide on silicon hexachloride, a compound, $Si_6H_6O_{12}Me_3$, is obtained, which yields 102—118 c.c. of hydrogen per gram of substance when decomposed with potassium hydroxide. Under other experimental conditions, compounds $Si_6H_2O_{12}Me_4$, $Si_6HO_{11}Me_5$, and $Si_6H_2O_7Me_8$ are obtained; these yield less and less hydrogen on decomposition as the number of methyl groups increases.

Hexamethylsilicoethane, Si_2Me_6 (Bygden, A., 1912, i, 341), does not yield hydrogen on decomposition, although containing the linking Si—Si. Evidently the characteristic decomposition of silicon

compounds with alkali hydroxide is due to the association of oxygen complexes with the silicon atoms. E. F. A.

The Isolation and Properties of Some Electropositive Groups and their Bearing on the Problem of the Metallic State. Charles A. Kraus (*J. Amer. Chem. Soc.*, 1913, **35**, 1732—1741).—When solutions of mercury alkyl salts in liquid ammonia are electrolysed, the free mercury alkyl group is deposited at the cathode, except in the case of members of the series above C_4H_9Hg, when no deposition takes place. The electrolytic cell used contained small platinum wires as electrodes, the cathode being situated at the bottom of the cell. The free groups deposited as an attenuated, opaque mass, which, by means of pressure, could be brought into a fairly coherent form. They are good conductors of electricity and do not amalgamate with mercury to any extent.

The *mercury methyl group*, $HgCH_3$, was obtained pure from the compound MeHgCl by washing it free from salt with liquid ammonia. Decomposition takes place at ordinary temperatures, with the formation of mercury and mercury methyl, $HgMe_2$; there is appreciable decomposition at $-33°$. The ethyl derivative behaves similarly, but the propyl derivative is less stable. The ethyl mercury group, when compressed, exhibits metallic reflection of a copper colour, whereas the mercury methyl group is black.

Attempts to isolate groups by the electrolysis of liquid ammonia solutions of the following salts were not successful: Me_4SbI, Me_3SI, Ph_2II, $C_5H_{11}HgI$, $C_8H_{17}HgI$, PhHgI, and Me_3SnI.

The bearing of the above results on the metallic state is discussed, and the conclusion drawn that the electrons to which conduction is due in metals are the same electrons which are involved in the common chemical combination of metals with other elements.

T. S. P.

The Optical Activity of Petroleum and its Significance. Frank W. Bushong (*Science*, 1913, **38**, 39—44).—Attention is drawn to the optical activity of the heavy oils. Since the naphthenic acids derived from the petroleum by treatment with alkali during refining are optically active, the activity of the original oil might be attributed to these acids. It does not necessarily follow, however, that the optically active constituents present in these naphthenic acids are identical with those originally present in the petroleum, and there seems good evidence that this is not the case, as both the author and others have found that the heavy oils retain most of their optical activity after treatment with alcoholic potash; still, the optical activity may be due to some extent to these acids. It is probable that the oils contain active hydrocarbons (naphthenes), and it is generally held that the naphthenic acids are oxidation products of these.

[The author's views as to the cause of the activity of petroleum were somewhat misrepresented in an earlier abstract (this vol., i, 969).]

J. C. W.

Distillation of Coal under Reduced Pressure. AMÉ PICTET and MAURICE BOUVIER (*Ber.*, 1913, **46**, 3342—3353; *Compt. rend.*, 1913, **157**, 779—781).—In an earlier paper (Pictet and Ramseyer, A., 1911, i, 850) it has been shown that extraction of coal (Montrambert) with boiling benzene gives a mixture of hydroaromatic hydrocarbons, from which a hexahydrofluorene, $C_{13}H_{16}$, could be isolated; it was also mentioned that distillation of the same coal under reduced pressure produced a similar mixture in which the same hydrocarbon could be detected. As the latter procedure was more rapid and gave better yields, it has now been applied more carefully.

The method was to heat 2—5 kilograms of the coal in a vertical iron retort of approximately 10 litres capacity; the temperature was slowly raised to 450°, whilst the pressure was maintained at a few centimetres of mercury by means of water-pumps. The experiment generally occupied about five hours.

Of the products of the decomposition, the tar only was carefully investigated; the gases were not collected, but were observed to resemble butadiene and isoprene in odour; the water had an acid reaction and contained no ammonium salts; the coke was found to yield still further quantities of combustible gas when heated more strongly. The tar, which amounted to approximately 4% of the coal, was lighter than water, had a brown colour with feeble green fluorescence, and resembled petroleum in odour; it contained no phenols, but a considerable quantity of bases which appeared to be mainly of the secondary type. Careful fractionation under reduced pressure failed to disclose the presence of any solid substances, and oxidation yielded only aliphatic acids, indicating the absence of aromatic hydrocarbons. It is therefore probable that the tar is a mixture of hydroaromatic compounds of the naphthene class.

Decomposition of the crude tar by distillation at ordinary pressure through a red-hot iron tube packed with coke produced a considerable quantity of gas resembling coal gas in odour, and consisting mainly of hydrogen and paraffin hydrocarbons together with water containing much free ammonia and a dark-coloured tar resembling coal-tar in odour. This tar, unlike the original product, contained phenols, bases recalling the odour of pyridine, and aromatic hydrocarbons, amongst which benzene, naphthalene, and anthracene could be identified. It is tentatively suggested that in coal distillation the methane, ammonia, phenols, and aromatic hydrocarbons are not primary products, but are formed by the decomposition of intermediate products represented by the above "vacuum tar."

Treatment of certain fractions of the "vacuum tar" with sodium removes certain hydroxy-compounds (the presence of which had already been indicated by the results of analysis) which exhibit the usual behaviour of alcohols towards alkalis and acyl chlorides. The natural supposition that these alcohols form the origin of the phenolic substances during subsequent decomposition by further heat received no confirmation when they were passed in the vapourous condition through a red-hot tube, the only products being unsaturated hydrocarbons.

The hydrocarbon residues after extracting various fractions with

sodium immediately decolorise cold potassium permanganate solution, and consequently must contain unsaturated hydrocarbons. The latter were removed by the action of fuming sulphuric acid, and the residue again heated with sodium. By repeated fractional distillation the liquid was separated into various portions in the hope of identifying some of the constituents. Decahydronaphthalene was definitely proved to be absent, and a comparison of the compositions and densities of the various fractions with those of corresponding fractions from Caucasian petroleum clearly demonstrated their distinct character. A similar comparison with fractions from Canadian petroleum (which is also known to contain hydrocarbons of the general formula C_nH_{2n}) proved the identity of the fractions containing the hydrocarbons $C_{10}H_{20}$ and $C_{11}H_{22}$. The former of these is very sensitive to most reagents, and generally gives complex reaction products, but by the action of bromine vapour, dibromodurene (?), m. p. 202°, could be obtained; also by distillation over iron oxide at a dull red heat a distillate is obtained, which on nitration yields dinitrodurene(?), m. p. 202°. Although this evidence is not regarded as final, the authors consider themselves justified in identifying the hydrocarbon, $C_{10}H_{20}$, with hexahydrodurene (*s*-tetramethyl*cyclo*hexane), whilst to the hydrocarbon, $C_{11}H_{22}$, they ascribe the structure of a pentamethyl*cyclo*hexane. D. F. T.

Electrolytic Oxidation of Toluene. FRITZ FICHTER (*Zeitsch. Elektrochem.*, 1913, **19**, 781—784).—A suspension of toluene in 2*N*-sulphuric acid is placed in a large cylindrical lead vessel which serves as anode; a cathode consisting of a lead spiral is used. The suspension is vigorously stirred, and a current of 0·01 ampere per sq. cm. of anode is passed through until one-half of the toluene has disappeared. Stopping the process at this point, prevents the destruction of some of the products by further oxidation. The toluene layer on allowing it to settle contains after the oxidation toluquinone and a little benzaldehyde, whilst the aqueous layer contains quinol and phenol.

The process of the reaction proceeds as indicated:

$$CH_3{\cdot}C_6H_5 \begin{cases} \nearrow HO{\cdot}C_6H_4{\cdot}CH_3\ (1:2) \longrightarrow \\ \rightarrow HO{\cdot}C_6H_4{\cdot}CH_3\ (1:4) \longrightarrow \\ \searrow C_6H_5{\cdot}CHO \end{cases}$$

$$(HO)_2C_6H_3{\cdot}CH_3\ (1:2:5) \longrightarrow CH_3{\cdot}C_6H_3O_2$$

$$HO{\cdot}C_6H_3{\cdot}CHO\ (1:4) \begin{cases} \nearrow C_6H_4(OH)_2\ (1:4) \\ \searrow C_6H_5{\cdot}OH \end{cases}$$

It is thus obvious that the oxidation occurs mainly in the nucleus (compare also T. Kempf, A., 1901, i, 728; R. Kempf, A., 1911, i, 464). J. F. S.

Transformations of Unsaturated Haloid Compounds. II. Cinnamaldehyde and Phenyl Vinyl Ketone. FRITZ STRAUS and ABRAHAM BERKOW (*Annalen*, 1913, **401**, 121—159. Compare Straus, A., 1912, i, 989).—It has been shown (*loc. cit.*) that the changes R·CH:CH:CHR' ⟶ R·CH:CH·CO·R' ⟶ R·CO·CH:CHR' can be effected by a series of substitutive reactions. The present paper deals with a simple case in which R' is hydrogen. The conversion of cinnamaldehyde into phenyl vinyl ketone has been accomplished, but the reverse change of the ketone to the aldehyde has revealed unexpected and important peculiarities.

Cinnamaldehyde and phosphorus pentachloride readily yield the normal keto-chloride, cinnamylidene dichloride (*loc. cit.*), an ethereal solution of which reacts with a slight excess (over 1 mol.) of sodium methoxide to form *α-chloro-γ-methoxy-γ-phenyl-Δ^{α}-propene*,

CHCl:CH·CHPh·OMe,

b. p. 111°/18 mm., D_4^{15} 1·0959. The latter is converted in petroleum solution in the presence of calcium chloride into cinnamylidene dichloride by hydrogen chloride, yields cinnamaldehyde by hydrolysis, and is oxidised to α-methoxyphenylacetic acid by potassium permanganate in acetone. *α-Chloro-γ-ethoxy-γ-phenyl-Δ^{α}-propene*, $C_{11}H_{13}OCl$, b. p. 120·5°/12 mm., is prepared similarly. An ethereal solution of cinnamylidene dichloride and *N*-sodium hydroxide ($1\frac{1}{2}$ mols.) yields after a hundred and twenty hours a substance which loses water by distillation in a vacuum, and is converted into *γ-chloro-α-phenylallyl ether*, (CHCl:CH·CHPh)$_2$O, b. p. 127°/18 mm.

The *acetal* of phenyl vinyl ketone, CH_2:CH·CPh(OMe)$_2$, b. p. 85—86°/12 mm., D_4^{15} 0·9887, is obtained by boiling α-chloro-γ-methoxy-γ-phenyl-Δ^{α}-propene with 5% methyl-alcoholic sodium methoxide (2 mols.) for four days. The constitution of the acetal is proved by reduction by colloidal palladium and hydrogen at 2 atmospheres, whereby the *acetal*, b. p. 206—208° or 92—93°/18 mm., of phenyl ethyl ketone is obtained. The hydrolysis of the unsaturated acetal to phenyl vinyl ketone is difficult on account of the instability of the ketone, and has only been effected by means of 5% sulphuric acid at 60—70° in the absence of light.

Phosphorus pentachloride ($1\frac{1}{2}$ mols.) reacts with phenyl vinyl ketone in benzene to form *αγ-dichloro-α-phenyl-Δ^{α}-propene*, CPhCl:CH·CH_2Cl, b. p. 124—125°/16 mm., the constitution of which is proved by the action of ozone, followed by that of water, on the substance in carbon tetrachloride, whereby, amongst other products, benzoic and chloroacetic acids are obtained. The substance reacts with a slight excess (over 1 mol.) of methyl-alcoholic sodium methoxide to form quantitatively *α-chloro-γ-methoxy-α-phenyl-Δ^{α}-propene*, CPhCl:CH·CH_2·OMe, b. p. 131—132°/27 mm., D_4^{22} 1·146, which is reconverted into αγ-dichloro-α-phenyl-Δ^{α}-propene by hydrogen chloride in petroleum in the presence of calcium chloride, and yields benzoic acid by oxidation in acetone with potassium permanganate. By reduction in acetone with colloidal palladium and hydrogen at 2 atmospheres, α-chloro-γ-methoxy-α-phenyl-Δ^{α}-propene is converted into *methyl γ-phenylpropyl ether*,

CH_2Ph·CH_2·CH_2·OMe,

b. p. 207—208° or 92—94°/12 mm., D_4^{15} 0·9990, which has also been prepared from γ-phenylpropyl chloride and an excess of boiling sodium methoxide; *methyl α-phenylpropyl ether*, OMe·CHPhEt, prepared from α-phenylpropyl chloride in a similar manner, has b. p. 183—185° or 76—77°/14 mm., D_4^{15} 0·9216, and a quite different odour.

By boiling for four and a half to five days with 5% sodium methoxide, α-chloro-γ-methoxy-α-phenyl-Δ^{α}-propene is converted, unexpectedly, into *αγ-dimethoxy-α-phenyl-Δ^{α}-propene*,

$$OMe\cdot CPh:CH\cdot CH_2\cdot OMe,$$

b. p. 100—102°/11 mm., D_4^{15} 1·0412, which yields benzoic acid by oxidation in acetone by potassium permanganate, and is reduced by hydrogen and colloidal palladium to *αγ-dimethoxy-α-phenylpropane*, $OMe\cdot CHPh\cdot CH_2\cdot CH_2\cdot OMe$, b. p. 215—217° (decomp.) or 94—95°/15 mm., D_4^{15} 0·9829. The last substance has also been prepared from γ-chloro-α-phenylpropyl alcohol (Fourneau, A., 1907, i, 762); the chlorohydrin in benzene in the presence of calcium bromide is converted by hydrogen bromide into *γ-chloro-α-bromo-α-phenylpropane*, $CHPhBr\cdot CH_2\cdot CH_2Cl$, b. p. 118—120°/20 mm., which is converted by sodium methoxide successively into *γ-chloro-α-methoxy-α-phenylpropane*, $C_{10}H_{13}OCl$, b. p. 110—112°/12 mm., and αγ-dimethoxy-α-phenylpropane. C. S.

p-Nitrophenylethyl Chloride [β-Chloro-4-nitroethylbenzene]. JULIUS VON BRAUN and B. BARTSCH (*Ber.*, 1913, **46**, 3050—3055).—The product obtained by nitrating β-chloroethylbenzene can be separated into two portions, of which one is solid, the other liquid. The former, which may constitute 50% of the mixture, has been shown to be β-chloro-4-nitroethylbenzene (A., 1912, i, 498). The latter is now shown to have a similar constitution, since, on nitration, each substance yields *β-chloro-2-nitro-4-aminoethylbenzene*, which can be further reduced to *β-chloro-2 : 4-diaminoethylbenzene*, whilst, under the influence of sodium acetate and glacial acetic acid, each substance is transformed into a mixture of *4-nitro-β-acetoxyethylbenzene*, $NO_2\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot OAc$ and *4-nitro-α-acetoxyethylbenzene*,

$$NO_2\cdot C_6H_4\cdot CHMe\cdot OAc,$$

from which, on saponification, the corresponding alcohols are obtained. The formation of the latter substance probably depends on the intermediate production of 4-nitrostyrene, $NO_2\cdot C_6H_4\cdot CH:CH_2$. A similar reaction is not observed to any extent with β-chloroethylbenzene or γ-chloronitropropylbenzene.

β-Chloro-2-nitro-4-aminoethylbenzene, m. p. 84°, is obtained by the action of nitric and sulphuric acids on the hydrochloride of β-chloro-4-aminoethylbenzene obtained from solid β-chloro-4-nitroethylbenzene (compare A., 1912, i, 498). The *hydrochloride*, m. p. 190°, and the *benzoyl* derivative, m. p. 130°, have been prepared. Identical products are obtained from liquid β-chloro-4-nitroethylbenzene. Reduction of β-chloro-2-nitro-4-aminoethylbenzene (whether obtained from solid or liquid β-chloro-4-nitroethylbenzene) by means of stannous chloride gives *β-chloro-2 : 4-diaminoethylbenzene hydrochloride*, m. p. 256°, after darkening at 250°. The colour reactions of this salt greatly

resemble those of tolylenediamine. The free base has not been isolated.

When solid β-chloro-4-nitroethylbenzene is heated with sodium acetate and glacial acetic acid and the product fractionated under diminished pressure, two substances are obtained, b. p. 189°/16 mm. and 161—163°/16 mm. respectively. The former consists of 4-nitro-β-acetoxyethylbenzene [4-nitrobenzylcarbinyl acetate], and is converted by saponification into *4-nitro-β-hydroxyethylbenzene* [*4-nitrobenzylcarbinol*], $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot OH$, b. p. 177°/16 mm. (*benzoyl* derivative is oily; m-*nitrobenzoyl* derivative, m. p. 64—65°; *phenylurethane*, m. p. 127—128°), the constitution of which is proved by its conversion into β-chloro-4-nitroethylbenzene, 66% of which is obtained in the solid form. The fraction of lower b. p., consisting of α-acetoxy-4-nitroethylbenzene, yields the corresponding *alcohol*, b. p. 158°/16 mm. (*m-nitrobenzoyl* derivative, m. p. 152—153°; *phenylurethane*, m. p. 205—206°), which, on oxidation, gives *p*-nitrobenzoic acid. If the above operations are repeated with liquid β-chloro-4-nitroethylbenzene, the same products result and in the same yields.

β-Chloroethylbenzene, when treated with sodium acetate and acetic anhydride, gives an 85% yield of benzylcarbinyl acetate, b. p. 232°, which, on saponification, regenerates the alcohol. About 15% of *α-acetoxyethylbenzene*, b. p. 222°, is simultaneously produced, which loses some acetic acid on distillation and is saponified to phenylmethylcarbinol, b. p. 204°.

γ-Acetoxy-4-nitropropylbenzene, b. p. 210—212°/21 mm. (slight decomp.), is obtained as sole product of the action of acetic acid and sodium acetate on γ-chloro-4-nitropropylbenzene. H. W.

Spectrochemical Notes. I. Hydrated Naphthalenes. II. Spectrochemical Behaviour of Acenaphthene Derivatives. III. Haworth's Dimethyl*cyclo*hexadiene. KARL VON AUWERS (*Ber.*, 1913, 46, 2988—2995).—Δ^1-Dihydronaphthalene and Δ^2-dihydronaphthalene (Straus and Lemmel, this vol., i, 256) have $D_4^{\cdot}$ 0·9982, $n_D^{\cdot 1}$ 1·58326, and $D_4^{\cdot 7}$ 0·9928, $n_D^{\cdot 7}$ 1·55489 respectively.

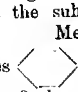
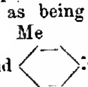
The 1:2:3:4-tetrahydronaphthalene obtained by von Braun and Deutsch (A., 1912, i, 435) is apparently not a homogeneous product, but the specimens obtained by Willstätter and King (this vol., i, 353) and by Straus and Lemmel (*loc. cit.*) agreed together in their properties, namely, $D_4^{17\cdot8}$ 0·9738, $n_D^{17\cdot8}$ 1·54529.

Decahydronaphthalene (Willstätter and King, *loc. cit.*) gave $D_4^{\cdot}$ 0·8951, $n_D^{\cdot 0}$ 1·48035.

A comparison of the refractive indices for various wave-lengths indicates that, of the above substances, Δ^1-dihydronaphthalene alone has high exaltation of specific refraction and dispersion; *cyclo*hexadiene is remarkable for showing a slight depression, a phenomenon which has also been observed with *cyclo*hexene. Tetrahydronaphthalene gives results in accord with those expected for a di-substituted benzene derivative, and decahydronaphthalene is approximately normal.

In connexion with the work of Crompton and Smyth (T., 1913, 103, 1302), who come to the decision that acenaphthene and its

mono halogen derivatives are optically normal, attention is drawn to the fact that their calculations are made with the molecular refraction of naphthalene as a standard. As this substance exhibits a marked exaltation, it follows that the acenaphthene compounds are also optically exalted.

In reference to the two compounds described as dimethylcyclohexadienes (Haworth, T., 1913, **103**, 1242), one of which has already been prepared (Murawski, *Diss.*, Greifswald, 1911), the author, on optical and also chemical grounds (compare Auwers and Peters, A., 1910, i, 826), regards the substances as being at least mainly composed of the substances $:CH_2$ and $:CH_2$ respectively.

1 : 3-*Dimethyl*cyclo-Δ^1-*hexen-3-ol*, which Haworth failed to isolate as the intermediate product in the preparation of the latter of the above two substances, can be obtained from 1-methyl*cyclo*-Δ^1-hexen-3-one by the action of magnesium methyl iodide; it has b. p. 75°/15 mm., $D_4^{16\cdot4}$ 0·9336, $n_D^{16\cdot5}$ 1·47711. D. F. T.

Organic Radicles. XVIII. Ditertiary Hydrazines. HEINRICH WIELAND and CARL MÜLLER (*Annalen*, 1913, **401**, 233—243).—The dissociation of tetra-anisylhydrazine in solution into the free radicles $\cdot N(C_6H_4\cdot OMe)_2$ (A., 1912, i, 907) is found to be in harmony with Piccard's colorimetric dilution law (A., 1911, ii, 561).

An interesting contribution to the chemistry of triphenylmethyl is recorded. When heated in boiling *m*-xylene, triphenylmethyl is converted into triphenylmethane and *p*-benzhydryltetraphenylmethane. In boiling *o*-xylene in an atmosphere of carbon dioxide, however, the products are triphenylmethane and a *triphenyl*-o-*xylylmethane*, $CPh_3\cdot C_6H_3Me_2$, m. p. 165—168°, colourless leaflets. In boiling *p*-xylene, similar results are obtained, triphenylmethane and *triphenyl*-p-*xylylmethane*, m. p. 158—159°, long prisms, being formed. These two hydrocarbons do not exhibit halochromy and, like tetraphenylmethane itself, develop intense yellow colorations with concentrated sulphuric acid and a trace of potassium dichromate.

Triphenylmethyl in benzene and triphenylmethyl peroxide in glacial acetic acid are reduced to triphenylmethane by hydrogen and palladium black. Triphenylmethyl and diphenylketen do not react in benzene at 60—70°. C. S.

Constitution and Colour. III. FRIEDRICH KEHRMANN (*Ber.*, 1913, **46**, 3036—3040. Compare A., 1908, i, 699, 993).—The author gives a further explanation of his views on this subject. In the formation of salts from phenazine, phenanthraquinone and similar substances, where the change is accompanied by a marked change in colour, the author is of opinion that the chromophore undergoes modification, for example, by an increase in the valency of one of the elements (nitrogen, oxygen, etc.), or by a change from the ortho- to the para-configuration or vice-versâ.

In reference to the views of Willstätter and Piccard (A., 1908, i, 475), the author draws attention to a constitutive characteristic common

to the coloured salts of the triphenylmethane class and to Wurster's salts; both classes have the auxochrome outside the quinonoid portion of the molecule, so that both may, in a wide sense, be regarded as of meriquinonoid type. D. F. T.

Double Chlorides of Ferric and Ferrous Chloride with Some Aromatic Bases. RAPHAEL MONROE MCKENZIE (*Amer. Chem. J.*, 1913, 50, 308—335).—A number of double chlorides of ferrous and ferric iron with the hydrochlorides of aniline *o*-toluidine, *m*-toluidine, and *p*-toluidine have been prepared by adding the constituent substances together in hydrochloric acid solution, and evaporating over sulphuric acid and solid potassium hydroxide.

The following compounds are described: $FeCl_3,2NH_3PhCl$, crystallising in stout, green needles; $FeCl_3,2NH_3PhCl,H_2O$, crystallising in long, thin, very dark green needles; $FeCl_3,6NH_3PhCl$, crystallising in long, thin, orange-yellow, silky needles; $FeCl_3,6NH_3PhCl,2H_2O$, crystallising in orange needles; $FeCl_3,6NH_3(C_7H_7)Cl,3H_2O[1:2]$, forming brownish-yellow needle clusters; $FeCl_3,2NH_3(C_7H_7)Cl[1:3]$, forming shining yellow plates; $FeCl_3,3NH_3(C_7H_7)Cl[1:3]$: this substance is a viscid, fuming mass which is very deliquescent and could not be crystallised; $FeCl_3,3NH_3(C_7H_7)Cl[1:4]$: forming lustrous, red prisms or plates; $FeCl_2,2NH_3PhCl,2H_2O$, separates from hydrochloric acid in light yellow needles; $FeCl_2,3NH_3(C_7H_7)Cl,6H_2O[1:2]$, crystallising in long, fine, yellow needles, and $FeCl_2,6NH_3(C_7H_7)Cl,HCl,xH_2O[1:2]$: this salt was prepared in the absence of air. J. F. S.

Quaternary Ammonium Salts from Trimethylamine and Arylsulphonyl Chlorides. DANIEL VORLÄNDER and OTTO NOLTE (*Ber.*, 1913, 46, 3212—3228. Compare Kauffmann and Vorländer, A., 1910, i, 822).—When trimethylamine in aqueous solution is shaken with benzenesulphonyl chloride, a quaternary salt is formed, characterised by forming a sparingly soluble platinichloride which allows of the separation from trimethylammonium platinichloride (compare A., 1910, i, 822). *Benzenesulphonyltrimethylammonium chloride*, $SO_2Ph\cdot NMe_3Cl$, obtained by saturating the platinichloride with hydrogen sulphide, crystallises in long, flat colourless prisms, m. p. 185° (decomp.), which are optically anisotropic. The *platinichloride*, $(PhSO_2\cdot NMe_3)_2PtCl_6$, forms doubly refractive platelets or small, flat prisms, m. p. 215—220° (decomp.). The *aurichloride*, $SO_2Ph\cdot NMe_3\cdot AuCl_4$, yields yellow, doubly refractive needles, m. p. 194—200°. The *picrate* crystallises in splendid, yellow, anisotropic plates and stellate aggregates, m. p. 137°. The *dichromate* is characterised by doubly refractive, orange-yellow crystals, m. p. 202°. The *perchlorate* forms colourless needles, m. p. 145°. The colourless needles of the *stannichloride* have decomp. 245°. The *thallichloride* likewise forms colourless, double refractive needles.

Toluene-p-sulphonyltrimethylammonium platinichloride separates in optically anisotropic platelets and pointed needles. The *dichromate* forms doubly refractive, orange-red plates, decomp. 195°.

Cryptocrystalline α- and *β-naphthalenesulphonyltrimethylammonium platinichlorides* were obtained.

Similar salts were not obtained from triethyl- or tripropyl-amine or from dimethyl- or diethyl-aniline.

The existence of these neutral benzenesulphonylammonium salts, stable towards water, which yet contain the very strongly acid benzenesulphonyl radicle, proves that the salt-forming function of the ammonium does not depend on the positive and negative nature of the radicles. E. F. A.

Catalysis on the Basis of Work with Imino-esters. The Problem of Saponification and Esterification. JULIUS STIEGLITZ (*J. Amer. Chem. Soc.*, 1913, **35**, 1774—1779).—A theoretical consideration of the mode of action of acids in accelerating the formation or hydrolysis of esters (compare A., 1908, ii, 29, 167, 472; this vol., ii, 396). Although purely mathematical considerations fail to decide with which oxygen compound (for example, acid or alcohol in esterification) the complex oxonium ion is produced, some decision can be drawn by analogy to the conversion of imino-esters by ammonia or amines into amidines which is also accelerated by acid. In this case the change may occur by interaction of the ammonium ion with the free imino-ester or of the imino-ester cation with free ammonia, according to the alternative schemes: $CPh(:NH)\cdot OMe + H\cdot NH_3^+ \longrightarrow$

$CPh\cdot C(NH_2)(OMe)\cdot NH_3^+ \longrightarrow CPh(:NH)\cdot NH_3^+ + MeOH$

or $CPh(OMe):NH_2^+ + HNH_2 \longrightarrow CPh(NH_2)(OMe)NH_3^+ \longrightarrow$ $CPh\cdot C(:NH)NH_3^+ + MeOH$. According to the latter scheme the salts of tertiary amines should be unable to form amidines from imino-esters, and according to Pinner this is actually the case.

The conclusion is therefore to be drawn that in the formation of amidines from imino-esters and amines in the presence of acids, action occurs between the amine (or ammonia) and the ion resulting from the additive compound of the imino-ester with the acid. Extending this analogy to the hydrolysis or formation of esters, it is in these cases most probable that the action is of a hydroxide, water, or alcohol on the oxonium ion of the ester or of the organic acid. D. F. T.

Hydrates of Calcium Oxide and their Molecular Compounds. IV. Compounds of Hydrated Calcium Oxide with Phenols. FEDOR F. SELIVANOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1535—1556. Compare this vol., ii, 214, 406, 407).—The following compounds of calcium hydroxide with phenol have been prepared.

The *diphenolate*, $CaO,H_2O,2PhOH$, apparently analogous to the barium compound obtained by Laurent (*Ann. Chim. Phys.*, 1841, [iii], 3, 203), is a colourless, hygroscopic compound, and is decomposed by carbon dioxide, although it remains unchanged in a sealed, exhausted tube. It is decomposed by water, with liberation of phenol and calcium hydroxide, a similar action being brought about by ether, benzene, alcohol, etc. On this ground the compound is regarded as possessing the constitution $Ca(OH)_2,2PhOH$, which is confirmed by the mode of dissociation of the diphenolate in a vacuum; the phenol is hence present as phenol of crystallisation, the water possessing a constitutional character. When heated

[illegible] 110°, the diphenolate is decomposed into phenol, water, and the monophenoxide, HO·Ca·OPh, in which the acid properties of the phenol are very faint, so that water effects decomposition into calcium hydroxide and phenol.

The diphenolate forms various hydrates, which may be expressed by the general formula $2Ca(OH)_2,4PhOH,(2n+1)H_2O$, where $n=$ 0, 1, 2, 3 or 4.

The diphenolate is capable of combining with phenol, giving the *tetraphenolate*, $Ca(OH)_2,4PhOH$, and the *hexaphenolate*,

$$Ca(OH)_2,6PhOH.$$

Calcium hydroxido and phenol are also able to form hygroscopic solid solutions, which separate in needles apparently of the rhombic system, and do not dissolve in water, but give with it an oily and an aqueous layer (compare Runge, *Ann. Phys. Chem.*, 1834, **31**, 69; **32**, 308) exhibiting an alkaline reaction. Similar solid solutions are formed by calcium hydroxide and thymol and by magnesium hydroxide and phenol. T. H. P.

Introduction of Selenium into Organic Compounds. Emil Fromm and Karl Martin (*Annalen*, 1913, **401**, 177—188).—Selenium, unlike sulphur, does not react with stilbene or ethyl cinnamate even by prolonged heating at high temperatures. Contrary to Bauer's statement (this vol., i, 263), 1-phenylbenzoselenazole is obtained in 15—20% yield by vigorously boiling benzanilide and selenium. It is not ruptured by fusion with potassium hydroxide, and forms a *tetrabromide*, $C_{13}H_9NBr_4Se$, m. p. 134°, brick-red powder, and a *tetraiodide*, $C_{13}H_9NI_4Se$, m. p. 84°, greenish-black, metallic crystals, with bromine and with iodine in cold and in boiling chloroform respectively. The four halogen atoms are very easily removed, so the substances probably have the constitution : $C_6H_4<\begin{smallmatrix}NX_2\\SeX_2\end{smallmatrix}>CPh$.

Equivalent quantities of potassium selenocyanate and *o*-nitrobenzyl chloride in boiling alcohol yield *o-nitrobenzyl selenocyanate*, $C_8H_6O_2N_2Se$, m. p. 77°, decomp. 215°, pale yellow crystals. *o*- and *p*-Chloronitrobenzenes do not react similarly, but 1-chloro-2:4-dinitrobenzene rapidly yields 2:4-*dinitrophenyl selenocyanate*, m. p. 163°, yellow crystals, which can be crystallised from concentrated nitric acid. 2:4-Dinitrophenyl selenocyanato and boiling aqueous alkalis yield a brownish-red solution containing the 2:4-dinitrophenylselenol, from which by atmospheric oxidation *di-2:4-dinitrophenyl diselenide*, $C_{12}H_6O_8N_4Se_2$, m. p. 264—265°, yellow crystals, is precipitated.

Dibenzyl diselenide, like dibenzyl disulphide (this vol., i, 357), reacts additively with bromine and iodine in chloroform to form a *tetrabromide*, $C_{14}H_{14}Br_4Se_2$, m. p. 137°, red powder, and *tetraiodide*, m. p. [illegible]°, dark green, metallic crystals; the additive compounds react with silver oxido or acetate, but are thereby extensively changed, and, unlike the corresponding disulphides (*loc. cit.*), do not yield the diselenoxide.

Seleno ethers are readily obtained by boiling dibenzyl diselenide with alcoholic sodium ethoxide (2 equiv.) and treating the resulting brownish-red solution of the selenol with an alkyl haloid. Thus

benzyl chloride yields Jackson's dibenzyl selenide, m. p. 45·5°, whilst methyl iodide, ethyl iodide, and ethylene dibromide yield respectively benzyl methyl selenide, benzyl ethyl selenide, and *dibenzyl ethylene selenide*, $C_2H_4(Se\cdot C_7H_7)_2$, m. p. 68—69°, pale yellow needles. Dibenzyl selenide reacts in chloroform with bromine or iodine to form the *dibromide*, $SeBr_2(C_7H_7)_2$, m. p. 84°, red powder, and *di-iodide*, m. p. 97°, violet crystals, from which, however, the selenoxide cannot be obtained by the action of alkalis, or silver oxide or acetate.

The so-called dibenzyl selenide nitrate obtained by Jackson in 1875 by the action of nitric acid on dibenzyl selenide proves to be *tribenzylselenonium nitrate*, $(C_7H_7)_3Se\cdot NO_3$, decomp. 102—103°; the corresponding *chloride*, $C_{21}H_{21}ClSe$, has m. p. 92°. C. S.

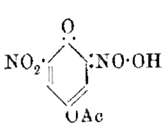
Nitroquinhydrones. M. M. RICHTER (*Ber.*, 1913, **46**, 3434—3438).—The author has previously pointed out (A., 1911, i, 136) that the introduction of negative groups into the quinone molecule diminishes the basic properties of the oxygen atom, and thus reduces the tendency to quinhydrone formation. In agreement with this view it is found that nitroquinol combines with *p*-benzoquinone to form an unstable quinhydrone, whilst in the case of 2 : 6-dinitroquinol the ability to give rise to quinhydrones has completely disappeared.

Nitroquinhydrone, $C_6H_4O_2,C_6H_3(OH)_2\cdot NO_2$, prepared by evaporating an ethereal solution of *p*-benzoquinone and nitroquinol in the absence of moisture, crystallises in small needles or stout, obliquely cut prisms. It is almost black, and has m. p. 89—90°, with slight previous decomposition at 84°. On exposure to air, it loses *p*-benzoquinone, yielding nitroquinol.

By nitrating the diacetyl derivative of quinol, Hesse (A., 1880, 317) and Nietzki (A., 1883, 465) have obtained a dinitro-derivative, m. p. 96°, which they consider to be the diacetyl derivative of 2 : 6-dinitroquinol. The author finds, however, that the substance is not a diacetate, but a monoacetyl derivative, one of the acetyl groups being removed during the nitration.

A similar elimination of an acetyl group occurs during the nitration of the diacetyl derivative of toluquinol.

On account of its yellow colour, the monoacetate is considered to be an aci-2 : 6-*dinitro-4-acetoxyphenol* of the annexed constitution. It has m. p. 95·6°, and on treatment with metallic nitrites in aqueous solution yields salts, which decompose explosively when heated. The *sodium* salt forms red needles, containing water (3 mols.), which is lost on exposure to sunlight, the anhydrous salt being orange in colour. The golden-yellow *barium* salt and red *potassium* salt (needles) are also described.



2 : 6-*Dinitro*-1 : 4-*diacetoxybenzene*, $C_6H_2(NO_2)_2(OAc)_2$, prepared by heating the preceding monoacetyl derivative or its sodium and potassium salts with acetic anhydride, crystallises in slender, colourless needles, m. p. 135°.

2 : 6 - *Dinitro* - 1 - *benzoyloxy-4-acetoxybenzene*, $OAc\cdot C_6H_2(NO_2)_2\cdot OBz$, obtained by the action of benzoyl chloride on the monoacetate is

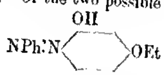
in acetone solution in the presence of pyridine, forms small, white needles, m. p. 128—129°.

2:6-Dinitroquinol and its monoacetyl derivative possess pronounced acid properties, and combine with aniline, toluidine, benzidine, diphenylformamidine, carbamido hydrazine and pyridine to form coloured additive compounds.

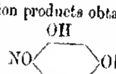
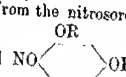
The additive *compound* of aniline with 2:6-dinitroquinol crystallises in dark red needles, m. p. 102—103° (decomp.).

The additive *compound* of aniline with *aci*-2:6-dinitro-4-acetoxyphenol forms orange needles, m. p. 120° (decomp.). F. B.

The Constitution of the Monomethyl and Monoethyl Ethers of Aminoresorcinol from the Monomethyl and Monoethyl Ether of Benzeneazo-4-resorcinol. FERDINAND HENRICH and H. BIRKNER (*Ber.*, 1913, **46**, 3380—3384).—The constitution of the ethyl ether obtained by the action of ethyl iodide on the potassium salt of benzeneazo-4-resorcinol has never been finally settled (Will and Pukall, A., 1887, 660). Of the two possible formulæ,



and , the former is rendered more probable by the work of Bechhold (A., 1889, 1155) on the corresponding methyl ether, but the evidence is far from satisfactory.

The reduction products obtained from the nitrosoresorcinol ethers of the structure  and , where R represents the methyl or ethyl radicle (Henrich and Rhodius, A., 1902, i, 447), will by comparison with the reduction products of the above azo-compounds fix definitely the constitution of the latter. Experiment shows that it is the o-amino-ether which is identical with the corresponding ether above, so that the first of the two possible formulæ for the ethyl (and methyl) ether is the correct one, alkylation having occurred in the para-position.

Improved methods are described for the methylation (by methyl sulphate) and ethylation of the benzeneazoresorcinol. D. F. T.

Action of Organomagnesium Derivatives on Trialkylacetophenones. (Mme.) PAULINE RAMART-LUCAS (*Ann. Chim. Phys.*, 1913, [viii], 30, 349—432).—The reaction between magnesium methyl, ethyl, phenyl, or benzyl haloid and trimethylacetophenone proceeds normally and leads to the formation of the tertiary alcohol,

$$CMe_3 \cdot CPhR \cdot OH.$$

Such carbinols do not exhibit ordinary alcoholic functions, and are readily dehydrated, yielding an unsaturated hydrocarbon. The individual compounds have been described (A., 1910, i, 378; 1911, i, 636; 1912, i, 351, 449). Magnesium propyl or *iso*propyl iodide acts

as a reducing agent to trimethylacetophenone and converts it into the corresponding secondary alcohol.

α-Phenyl-α-anisyl-ββ-dimethylpropan-α-ol,

$$CMe_3\cdot CPh(OH)\cdot C_6H_4\cdot OMe,$$

m. p. 67—68°, b. p. 210—215°/15 mm., and *α-phenyl-α-phenetyl-ββ-dimethylpropan-α-ol*, b. p. 215—220°/15 mm., have been prepared from trimethylacetophenone and magnesium anisyl or phenetyl bromide. The following alcohols have been obtained in a similar manner from αα-diethylpropiophenone or triethylacetophenone; the yields are generally smaller than those obtained with trimethylacetophenone. *β-Phenyl-γ-methyl-γ-ethylpentan-β-ol*, $CMeEt_2\cdot CPhMe\cdot OH$, b. p. 83—84°/3 mm., D_4^{25} 0·9781, $n_α$ 1·51692, n_D 1·52061, $n_β$ 1·529.., *αα-diphenyl-β-methyl-β-ethylbutan-α-ol*, $CMeEt_2\cdot CPh_2\cdot OH$, b. p. 200—205°/13 mm., D_4^{25} 0·95005, $n_α$ 1·56573, n_D 1·57206; by distillation at the ordinary pressure, the latter decomposes into benzophenone and γ-methylpontane. *αβ-Diphenyl-γ-methyl-γ-ethylpentan-β-ol*,

$$CMeEt_2\cdot CPh(OH)\cdot CH_2Ph,$$

b. p. 200—202°/15 mm., D_4^{25} 0·9791, $n_α$ 1·55249, n_D 1·556.., $n_γ$ 1·57944, yields deoxybenzoin and γ-methylpentane by distillation under atmospheric pressure. *β-Phenyl-γγ-diethylpentan-β-ol*,

$$CEt_3\cdot CPhMe\cdot OH,$$

b. p. 160°/18 mm., and *αα-diphenyl-ββ-diethylbutan-α-ol*,

$$CEt_3\cdot CPh_2\cdot OH,$$

m. p. 47—48°, b. p. 215—220°/17 mm., are described; the latter decomposes quantitatively into benzophenone and γ-ethylpentane by distillation at the ordinary pressure.

The preceding tertiary alcohols have been dehydrated by heating them with formic, oxalic, or dilute sulphuric acid, or, best, with a mixture of acetic anhydride and acetyl chloride; in some cases, the constitutions of the resulting hydrocarbons have been established by the examination of their products of oxidation. Alcohols which contain the group $OH\cdot \dot{C}Ph\cdot CH<$ yield hydrocarbons of the type $\cdot CPh{:}C<$, whilst alcohols which contain the group $>CMe\cdot CPh_2\cdot OH$ apparently yield a mixture of hydrocarbons of the types $>C\begin{array}{c}CH_2\\ \diagup\quad\diagdown\end{array}CPh_2$ and $>CPh\cdot CPh{:}CH_2$; hydrocarbons of the latter typo are produced owing to an intramolecular transformation preceding dehydration. β-Phenyl-γγ-dimethyl-$Δ^α$-butene, $CMe_3\cdot CPh{:}CH_2$, b. p. 88—92°/15 mm., D_4^{25} 0·88.., $n_α$ 1·49708, n_D 1·50133, $n_β$ 1·51185, $n_γ$ 1·52106, yields acetophenone or trimethylacetophenone by oxidation by chromic and acetic acids or by acidified potassium permanganate respectively. *γ-Phenyl-δδ-dimethyl-$Δ^β$-pentene*, $CMe_3\cdot CPh{:}CHMe$, b. p. 91—93°/12 mm., D_4^{25} 0·9061, $n_α$ 1·51100, n_D 1·51550, $n_β$ 1·52710, $n_γ$ 1·53776, yields trimethylacetophenone by oxidation. The dehydration of αα-diphonyl-γγ-dimethylpropan-α-ol yields a *substance*, b. p. 159—160°/11 mm., D_4^{25} 1·0031, n_D 1·57589, which is probably a mixture of 1 : 1-diphenyl-2 : 2-dimethyl*cyclo*propane and 1 : 2-diphenyl-1 : 2-dimethyl*cyclo*propane or βγ-diphenyl-γ-methyl-$Δ^α$-butene, since it yields both acetophenone and benzophenone by oxidation (A., 1912, i, 449). *αβ-Diphenyl-γγ-dimethyl-$Δ^α$-butene*, $CMe_3\cdot CPh{:}CHPh$, b. p. 164—165°/11 mm., yields benzo-

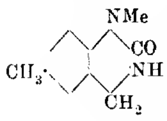
acid, trimethylacetophenone, and a *substance*, $C_{20}H_{20}O$, m. p. 131°, by oxidation. The dehydration of α-phenyl-α-anisyl-ββ-dimethylpropan-α-ol yields a liquid, b. p. 188—189°/15 mm., which is probably a mixture, since its products of oxidation contain *p*-anisic acid and *p*-methoxybenzophenone. Similar remarks apply to the liquid, b. p. 198—200°/15 mm., obtained by the dehydration of α-phenyl-α-phenetyl-ββ-dimethylpropan-α-ol. *αβ-Diphenyl-γ-methyl-γ-ethyl-Δ^α-pentene*, $CMeEt_2\cdot CPh\colon CHPh$, b. p. 175—180°/12 mm., D_4^{25} 0·9791, n_α 1·56110, n_D 1·56671, n_β 1·58131, n_γ 1·59467, yields benzoic acid, deoxybenzoin, and αα-diethylpropiophenone by oxidation. *β-Phenyl-γγ-diethyl-Δ^α-pentene*, $CEt_3\cdot CPh\colon CH_2$, b. p. 130—132°/15 mm., yields acetophenone and triethylacetophenone by oxidation. αα-Diphenyl-ββ-diethylbutan-α-ol is the only alcohol of the whole series which is not dehydrated by heating with acetic anhydride and acetyl chloride; the effect of this reagent, like that of boiling, is to decompose the alcohol into benzophenone and γ-ethylpentane.

Further attempts have been made to ascertain the constitution of the acid, $C_{17}H_{18}O_2$, m. p. 173° (*chloride*, $C_{16}H_{17}\cdot COCl$, m. p. 95—96°; *amide*, m. p. 149°), obtained ultimately from diphenyl-ψ-butylcarbinol (A., 1912, i, 623). From its method of formation the acid might be αβ-diphenyl-α-methylbutyric acid, ββ-diphenyl-αα-dimethylpropionic acid, or αα-diphenyl-β-methylbutyric acid; it is certainly not the first acid (*loc. cit.*). The last acid has been synthesised by the action of sodamide, followed by that of *iso*propyl iodide, on diphenylacetonitrile in boiling benzene; the resulting *αα-diphenyl-β-methylbutyronitrile*, $CPh_2Pr^\beta\cdot CN$, b. p. 193—195°/15 mm., is hydrolysed by acetic and hydrochloric acids at 180°, whereby are produced *αα-diphenyl-β-methylbutyric acid*, $CPh_2Pr^\beta\cdot CO_2H$, m. p. 166°, its *anhydride*, $C_{34}H_{34}O_3$, m. p. 162—163°, and a *substance*, $C_{16}H_{16}O_2$, m. p. 109—110°. The acid, $C_{17}H_{18}O_2$, m. p. 173°, therefore, is not αα-diphenyl-β-methylbutyric acid, neither is it ββ-diphenyl-αα-dimethylpropionic acid, m. p. 134—135°, which has been synthesised by Nef. C. S.

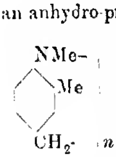
Tertiary Derivatives of *o*- and *p*-Aminobenzyl Alcohol. II. JULIUS VON BRAUN, O. KRUBER, and E. AUST (*Ber.*, 1913, **46**, 3056—3069).—It has been previously shown (A., 1912, i, 968) that the group $-CH_2\cdot OH$ can be introduced into tertiary aromatic amines by the use of an excess of formaldehyde. The present communication deals (1) with the reactivity of the tertiary, basic groups; (2) the possibility of replacing the hydrogen atoms of the benzene nucleus, and (3) the capacity for condensation of the hydroxyl group present in the side chain.

1. Tertiary aminobenzyl alcohols cannot be de-alkylated by means of cyanogen bromide, since the hydroxy-group is also affected. If the latter is protected, however, dealkylation is readily effected. Thus, when 6-dimethylamino-3-methylbenzyl acetate is treated with cyanogen bromide at the ordinary temperature during several days, 6-*cyanomethylamino-3-methylbenzyl acetate*, $CN\cdot NMe\cdot C_6H_3Me\cdot CH_2\cdot OAc$, b. p. 210°/10 mm., is obtained, whilst, in the same manner, the corresponding *cyano* compound, b. p. 213—216°/11 mm., is prepared from

4-dimethylamino-3-methylbenzyl acetate. Secondary aminobenzyl alcohols cannot be prepared by saponification of these compounds when the $-CH_2 \cdot OH$ is in the ortho- or para-position to the cyano-group. When 6-cyanomethylamino-3-methylbenzyl acetate is boiled with aqueous alcoholic sulphuric acid, a *base*, $C_{10}H_{12}ON_2$, b. p. 166—168°/8 mm., m. p. 59—60°, is obtained (*platinichloride*, m. p. 214°), which is probably a quinoxaline derivative of the annexed formula.

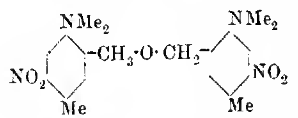


Under similar conditions, the cyano-group of 4-cyanomethylamino-3-methylbenzyl acetate is not replaced; concentrated hydrochloric acid at 120°, however, forms an amorphous *product*, which softens at 70°, and has m. p. 76—80°. It appears to be an anhydro-product of the secondary base (annexed formula), since it combines with dimethylaniline in hot, faintly acid solution to form *trimethyldiaminophenyltolylmethane*, m. p. 55°.



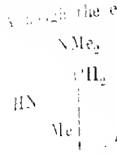
That 4-*methylamino*-3-*methylbenzyl alcohol* is capable of existence in the free state (unlike methyl-amino- and ethylamino-benzyl alcohols) is proved by its isolation from the products of the action of a large excess of formaldehyde on monomethyl-*o*-toluidine. It is a yellow oil, b. p. 130—132°/8 mm., which yields a *picrate*, m. p. 112°, and a platinichloride, reddish-yellow crystals, m. p. 173°.

II. 4-*Nitro*-6-*dimethylamino*-3-*methylbenzyl alcohol*, b. p. 191—192°/8 mm., m. p. 51° (*platinichloride*, m. p. 198°; *picrate*, m. p. 153°), is formed when a mixture of nitric and sulphuric acids is slowly added to a solution of 6-dimethylamino-3-methylbenzyl alcohol in concentrated sulphuric acid, the temperature being kept at 0° during two hours and the mixture subsequently being allowed to remain for three hours at the ordinary temperature. Should the temperature be allowed to rise, considerable quantities of a substance are formed which can be isolated in the form of its sparingly soluble *sulphate*.



The free *base* (annexed formula) has m. p. 136°, and is not hydrolysed by prolonged warming with $2N$-sulphuric acid. The *picrate* has m. p. 154°. 6-*Nitro*-4-*dimethylamino*-3-*methylbenzyl alcohol*, b. p. 204—208°/11 mm. (slight decomp.), m. p. 64—65° (*platinichloride*, reddish-yellow, crystalline powder), is similarly prepared from 4-dimethylamino-5-methylbenzyl alcohol.

4-Nitro-6-dimethylamino-3-methylbenzyl alcohol is readily reduced by stannous chloride and hydrochloric acid to 4-*amino*-6-*dimethylamino*-3-*methylbenzyl alcohol*, white crystals, m. p. 103—104°. The base is completely decomposed by distillation, yields a *picrate*, m. p. 179°, a viscous *acetyl* compound, and a *monobenzoyl* compound, m. p. 135°. It is slowly diazotised by nitrous acid. It combines with allylthiocarbimide, yielding the crystalline *compound*, $NMe_2 \cdot C_6H_2Me(CH_2 \cdot OH) \cdot NH \cdot CS \cdot NH \cdot C_3H_5$, m. p. 178°, and with salicylaldehyde, yielding the *salicylidene* compound, m. p. 7[illegible].



Although the composition of the base seems, therefore, to be firmly established, certain indications lead the authors to consider that there is some tendency for it to pass into the *anhydro*-compound (annexed formula) in the presence of aqueous mineral acids; thus the base, in itself colourless, dissolves in aqueous acid with a reddish-yellow coloration, whilst the colourless *hydrochloride* becomes yellow on exposure to moist air. Further, the base, like the readily dehydrated *p*-aminobenzyl alcohol and its monoalkyl derivatives and unlike the tertiary amino-alcohols in which dehydration is impossible, readily condenses with aromatic compounds in faintly acid solution to form derivatives of diphenylmethane. So with dimethylaniline, it yields 4-*amino-2′:4′-tetramethyldiamino-3-methyldiphenylmethane*, m. p. 92° (*benzoyl* derivative, m. p. 134°), whilst the correspooding *compound* from aniline is oily and gives a *diacetyl* derivative, m. p. 207°.

III. The condensation of dimethylaminobenzyl alcohol and its homologues with dimethylaniline and its homologues, which does not occur to an appreciable extent with aqueous acid solution, can be effected at higher temperatures by the help of zinc chloride. The authors have already shown that a derivative of diphenylmethane is then formed in the case of 4-dimethylaminobenzyl alcohol and dimethylaniline (A., 1912, i, 970), and now show by a series of examples that the reaction takes a similar course with their homologues containing methyl groups. Thus 4-dimethylaminobenzyl alcohol and dimethyl-*m*-toluidine yield 4 : 4′-*tetramethyldiaminophenyl-o-tolylmethane*, $NMe_2\cdot C_6H_4\cdot CH_2\cdot C_6H_3Me\cdot NMe_2$, b. p. 240—244°/8 mm. (*platinichloride*, m. p. 188—190° after darkening from 150°; *picrate*, m. p. about 70°), the constitution of which follows from its identity with the product obtained by the action of dimethyl-*m*-toluidine on 4-dimethylaminobenzyltoluidine in hydrochloric acid solution (compare Cohn and Fischer, A., 1900, i, 690).

Trimethyldiaminophenyl-*m*-tolylmethane (see above) is difficultly converted by exhaustive methylation into a pure di-quaternary iodide. When heated at 120° during three hours with methyl iodide and methyl alcohol, it yields a mono-*methiodide*, $C_{19}H_{27}N_2I$, m. p. 152°, which, when distilled in a vacuum, gives 4 : 4′-tetramethyldiaminophenyl-*m*-tolylmethane (obtained from 4-dimethylamino-3-methylbenzyl alcohol and dimethylaniline, A., 1912, i, 970), which is further identified by means of its picrate, m. p. 183°.

The statement of the D.R.-P. No. 107712, that aminobenzylaniline and its homologues only condense with amines which do not contain a substituent in the para-position is incorrect, at any rate as far as *p*-toluidine is concerned; when dimethylaminobenzyltoluidine is treated with *p*-toluidine in hydrochloric acid solution, 2′-*amino*-4-*dimethylaminophenyl*-m-*tolylmethane*, $NH_2\cdot C_6H_3Me\cdot CH_2\cdot C_6H_4\cdot NMe_2$, b. p. 240—245°/10 mm., m. p. 87°, is obtained in poor yield. The *picrate* has m. p. 180—181°. When heated with methyl iodide and methyl alcohol, the base yields a di-quaternary iodide, m. p. 204° (previously obtained from 2-dimethylamino-5-methylbenzyl alcohol and dimethyl-

aniline), which, when heated in a vacuum, yields 4 : 6′-tetramethyl-diaminophenyl-*m*-tolylmethane, m. p. 84°.

4-Dimethylamino-3-methylbenzyl alcohol condenses with dimethyl-*o*-toluidine to form *s-tetramethyldiaminodi*-m-*tolylmethane*,

$$CH_2(C_6H_3Me\cdot NMe_2)_2,$$

yellow oil, b. p. 228—229°/11 mm.; *picrate*, m. p. 187°; *platinichloride*, needles, m. p. 224° after darkening at 222°; *methiodide*, m. p. 19[illegible] after softening at about 190°. The constitution of the base is proved by its identity with the product obtained by the methylation of *s*-dimethyldiaminodi-*m*-tolylmethane prepared by Gnehm and Blumer by the condensation of formaldehyde with methyl-*o*-toluidine.

The liquid nature of many of the basic derivatives of diphenyl-methane and the frequently indistinct melting point of their salts has led the authors to investigate the suitability of their nitro-derivatives in characterising them. They seem to be generally well adapted for this purpose. According to the quantity of nitric acid used, mono- or di-nitro-derivatives can be obtained which are crystalline, and can readily be reduced by stannous chloride to the corresponding mono- and di-amino-compounds. In this connexion, the following substances have been prepared: 2 : 2′-*dinitro*-4 : 4′-*tetramethyldiaminodi*-m-*tolyl-methane*, $CH_2[C_6H_2Me(NO_2)\cdot NMe_2]_2$, yellow leaflets, m. p. 125°; 4 : 4′-dinitro-2 : 2′-tetramethyldiaminodi-*m*-tolylmethane, m. p. 102°, which, on reduction, yields the corresponding *di-amino*-compound. 2′ : 4-*dinitro*-2 : 4′-*tetramethyldiaminophenyl*-m-*tolylmethane*,

$$NMe_2\cdot C_6H_2Me(NO_2)\cdot CH_2\cdot C_6H_3(NO_2)\cdot NMe_2,$$

dark red crystals, m. p. 187°, which is reduced to the *diamino*-derivative, colourless crystals, m. p. 140°; 2′-*nitro*-2 : 4′-*tetramethyl-diaminophenyl*-m-*tolylmethane*, $NMe_2\cdot C_6H_3Me\cdot CH_2\cdot C_6H_3(NO_2)\cdot NMe_2$, red crystals, m. p. 94°; corresponding *amino*-compound, m. p. 97—98°.

According to Biehringer (A., 1897, i, 73), 2 : 2′-diamino-4 : 4′-tetra-methyldiaminodiphenylmethane loses ammonia when heated with hydrochloric acid with formation of an acridine ring. The authors find that a similar ring formation does not occur when the hydrogen atoms of the amino-group are replaced by methyl. When heated with hydrochloric acid at a temperature not exceeding 180°, the bases are unchanged; under more drastic treatment, formaldehyde is eliminated, but the liberation of methyl-, dimethyl- or trimethyl-amine could not be detected. H. W.

Tertiary Derivatives of *o*- and *p*-Aminobenzyl Alcohol. III. JULIUS VON BRAUN and OTTO KRUBER (*Ber.*, 1913, **46**, 3460—3470).—In previous papers (A., 1912, i, 968; preceding abstract), the authors have shown that tertiary aromatic amines of the dialkylaniline type readily condense with formaldehyde, either alone or in the presence of hydrochloric acid, yielding derivatives of 2 : 2′- and 4 : 4′-tetra-alkyl-diaminodiphenylmethane, $CH_2(C_6H_4\cdot NMe_2)_2$, and of *o*- and *p*-dialkyl-aminobenzyl alcohols. The reaction has now been extended to the following amines in order to ascertain the effect of nuclear substituents on the course of the condensation: (1) dimethyl-*m*-toluidine, (2) diethyl-*m*-toluidine, (3) dimethyl-*m*-chloroaniline, (4) phenylbenzyl-methylamine, (5) dimethylcumidine, (6) dimethyl-*p*-chloroaniline,

... dimethyl-*p*-bromoaniline, (8) dimethyl-*p*-bromo-*m*-toluidine, and dimethyl-*o*-chloroaniline.

The meta-substituted amines, (1) and (3), resemble the unsubstituted dimethylaniline in that they are almost quantitatively converted by the theoretical amount of formaldehyde ($\frac{1}{2}$ mol.) into the corresponding diphenylmethane derivatives, whilst, with excess of formaldehyde, only small yields of the dialkylaminobenzyl alcohols are obtained. The behaviour of the para-substituted amines (5)—(8) is similar to that of dimethyl-*p*-toluidine. They do not form diphenylmethane derivatives, but, with excess of the aldehyde, give rise to the dialkylaminobenzyl alcohols in good yield.

In the case of the amines 6, 7 and 8, containing a halogen atom in the para-position to the dimethylamino-group, the prolonged action of formaldehyde in the presence of hydrochloric acid causes partial oxidation of the alcohol to the corresponding acid.

It is also found that dimethyl-*o*-chloroaniline condenses with formaldehyde much more readily than dimethyl-*o*-toluidine, and the conclusion is, therefore, drawn that the inhibiting effect of ortho-substituents on the reactivity of the para-hydrogen atoms of the dialkylanilines is not always the same (compare Friedländer, A., 1899, i, 550), but may vary considerably with the nature of the substituent.

Dimethyl-*m*-toluidine condenses with formaldehyde ($\frac{1}{2}$ mol.), yielding 4 : 4'-tetramethyldiaminodi-*o*-tolylmethane, b. p. 253—256°/12 mm., m. p. 82° (*picrate*, m. p. 150°); with excess of formaldehyde it yields *4-dimethylamino-3-methylbenzyl alcohol* as a yellow, almost colourless oil, b. p. 138—142°/10 mm., which forms a *picrate*, felted needles, m. p. 145—146°, an oily *methiodide*, a *platinichloride*, needles, m. p. 178°, and *m-nitrobenzoyl* derivative, m. p. 64°.

4 : 4'-Tetraethyldiaminodi-o-tolylmethane, $CH_2(C_6H_3Me\cdot NEt_2)_2$, b. p. 260—266°/10 mm., m. p. 54—55°, and *4-diethylamino-3-methylbenzyl alcohol*, b. p. 160—170°/18 mm. (decomp.) are formed by condensing diethyl-*m*-toluidine with formaldehyde. The alcohol is very resistant towards reducing agents and forms a *picrate*, m. p. 100—103°; the *platinichloride* and *methiodide* are oils.

m-Chlorodimethylaniline condenses with formaldehyde ($\frac{1}{2}$ mol.) in the presence of hydrochloric acid, yielding *4 : 4'-tetramethyldiaminodichlorodiphenylmethane*, b. p. 272—276°/9 mm., m. p. 96—97° [*picrate*, m. p. 130—133°; *platinichloride* (decomp. 230°)], which on oxidation with lead dioxide is converted into *4 : 4'-tetramethyldiamino-2 : 2'-dichlorobenzhydrol*. This forms colourless crystals, m. p. 121°, yields blue solutions in glacial acetic acid, and condenses with dimethylaniline in acid solution to form *4 : 4' : 4''-hexamethyltriamino-2 : 2'-dichlorotriphenylmethane*, $NMe_2\cdot C_6H_4\cdot CH(C_6H_3Cl\cdot NMe_2)_2$, which separates from alcohol in lustrous crystals, m. p. 193°, and is oxidised to a blue *dye* of extraordinary fastness to light.

2-Chloro-4-dimethylaminobenzyl alcohol, obtained in poor yield (2%) from *m*-chlorodimethylaniline and excess of formaldehyde, forms a yellow oil, b. p. 156—160°/9 mm.; the *picrate* has m. p. 150°, the *platinichloride*, m. p. 184°.

p-Benzylmethylaminobenzyl alcohol, $C_7H_7\cdot NMe\cdot C_6H_4\cdot CH_2\cdot OH$, prepared from benzylmethylaniline, distils with decomposition at 230°

under diminished pressure, and, therefore, could not be isolated in a pure condition.

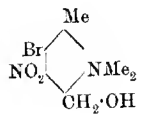
Dimethylcumidine gives rise to 6-*dimethylamino*-3-iso*propylbenzyl alcohol*, a yellow oil, b. p. 140—144°/8 mm. (*picrate*, m. p. 118—119°; *methiodide*, m. p. 147°; *platinichloride*, reddish-yellow leaflets, m. p. 187°), which condenses with 1-phenylpiperidine in the presence of zinc chloride, yielding 4-*piperidino*-6′-*dimethylamino*-3-iso*propyldiphenylmethane*, $NMe_2\cdot C_6H_3Pr^{\beta}\cdot CH_2\cdot C_6H_4\cdot NC_5H_{10}$, as a viscid oil, b. p. 260—266°/9 mm. (*picrate*, m. p. 100—105°; *platinichloride*, m. p. 219—220°).

Dimethyl-*p*-chloroaniline very readily condenses with formaldehyde, yielding 5-*chloro*-2-*dimethylaminobenzoic acid* (*hydrochloride*, m. p. 172—173°; *platinichloride*, m. p. 190°) and 5-*chloro*-2-*dimethylaminobenzyl alcohol*, a yellow oil, b. p. 158—160°/10 mm. (*picrate*, m. p. 152°; *methiodide*, m. p. 137°), which condenses with *p*-chlorodimethylaniline and dimethylaniline, yielding 5 : 5′-*dichloro*-2 : 2′-*tetramethyldiaminodiphenylmethane*, $CH_2(C_6H_3Cl\cdot NMe_2)_2$, b. p. 240—260°/14 mm., m. p. 151°, and 5-*chloro*-2 : 4′-*tetramethyldiaminodiphenylmethane*, b. p. 242—246°/12 mm., m. p. 144° (*picrate*, yellow leaflets, m. p. 165°; *methiodide*, m. p. 195°), respectively.

The behaviour of dimethyl-*p*-bromoaniline is similar, 5-*bromo*-2-*dimethylaminobenzoic acid* (not isolated) and 5-*bromo*-2-*dimethylaminobenzyl alcohol*, b. p. 160—170°/13 mm. (*picrate*, m. p. 153°) being produced.

By brominating dimethyl-*m*-toluidine, Wurster and Riedel (A., 1880, 109) obtained a bromo-compound of m. p. 98°, b. p. 276°. The authors find, however, that the bromination of pure dimethyl-*m*-toluidine in glacial acetic acid solution yields a bromo-derivative, m. p. 55°, b. p. 146—148°/17 mm., which decomposes completely on distillation under ordinary pressure. It forms a methiodide, m. p. 177°, identical with that described by Fischer and Windaus (A., 1900, i, 484) and accordingly must be a p-*bromodimethyl*-m-*toluidine*.

5-*Bromo*-2-*dimethylamino*-4-*methylbenzyl alcohol*, obtained together with the corresponding *acid* by the condensation of the preceding bromodimethyltoluidine with formaldehyde, has b. p. 168—172°/14 mm., forms a *picrate*, crystallising in leaflets, m. p. 150°, and on nitration in concentrated sulphuric acid solution yields a yellow, crystalline *nitro*-derivative, m. p. 83°, of the annexed constitution.



3-*Chloro*-4-*dimethylaminobenzyl alcohol*, b. p. 168—170°/11 mm. (*picrate*, m. p. 130°; *platinichloride*, m. p. 168°; *methiodide*, m. p. 119°; *nitro*-derivative, $C_9H_{11}O_3N_2Cl$, m. p. 80°), prepared from *o*-chlorodimethylaniline and excess of formaldehyde in the presence of hydrochloric acid, condenses with dimethylaniline and *o*-chlorodimethylaniline to form 3-*chloro*-4 : 4′-*tetramethyldiaminodiphenylmethane*, $NMe_2\cdot C_6H_3Cl\cdot CH_2\cdot C_6H_4\cdot NMe_2$, a liquid, b. p. 248—250°/12 mm. (*picrate*, m. p. 166—167°; *dimethiodide*, m. p. 201°), and 3 : 3′-*dichloro*-4 : 4′-*tetramethyldiaminodiphenylmethane*, $CH_2(C_6H_3Cl\cdot NMe_2)_2$, which forms a viscid oil, b. p.

235—240°/10 mm., yields a deep yellow *dinitro*-derivative, m. p. 144°, and is also obtained by the direct condensation of *o*-chlorodimethylaniline with the calculated amount of formaldehyde. F. B.

Steric Hindrance with Tertiary Aromatic Amines. JULIUS VON BRAUN and OTTO KRUBER (*Ber.*, 1913, **46**, 3470—3479).—In preparing the methiodides of the tetramethyldiaminodiarylmethanes, tabulated below, the authors found that the bases 5, 7, and 8, containing a substituent in the ortho-position to one of the dimethylamino-groups, combined rapidly with two molecules of methyl iodide, whilst in the case of the amines 2, 4, and 9, in which substituents occur in the ortho-position to both the dimethylamino-groups, the addition of methyl iodide proceeded very slowly. It would thus appear that the occurrence of the reaction at the sterically unhindered dimethylamino-group induces the same reaction at the sterically hindered group.

(1) 4:4'-Tetramethyldiaminodiphenylmethane.
(2) 4:4'-Tetramethyldiaminodi-*m*-tolylmethane.
(3) 4:4'-Tetramethyldiaminodi-*o*-tolylmethane.
(4) 6:6'-Tetramethyldiaminodi-*m*-tolylmethane.
(5) 4:4'-Tetramethyldiaminophenyl-*m*-tolylmethane.
(6) 4:4'-Tetramethyldiaminophenyl-*o*-tolylmethane.
(7) 4:6'-Tetramethyldiaminophenyl-*m*-tolylmethane.
(8) 4:4'-Tetramethyldiamino-*o*:*m*-ditolylmethane.
(9) 6:4'-Tetramethyldiaminodi-*m*-tolylmethane.
(10) 4:6'-Tetramethyldiamino-*o*:*m*-ditolylmethane.

The addition of methyl iodide to tertiary aromatic amines is, however, not particularly subject to steric influences, and the authors have, therefore, examined the behaviour of the above amines towards cyanogen bromide and iodoacetonitrile.

With respect to the action of cyanogen bromide on tertiary aromatic amines, it has already been shown that whilst sterically unhindered amines react with extreme ease at the ordinary temperature yielding compounds of the type $R\cdot NMe_3Br$ and $R\cdot NMe\cdot CN$, amines containing an ortho-substituent enter into reaction with great difficulty. In the case of iodoacetonitrile, the presence of an ortho-substituent completely suppresses the reaction.

In agreement with the results obtained by the addition of methyl iodide, it was found that the di-*o*-substituted amines 2, 4, and 9 do not react with either cyanogen bromide or iodoacetonitrile, whilst the amines 5, 7, 8, and 10, containing a substituent in the ortho-position to only one of the dimethylamino-groups, enter into reaction as readily as the amines 1, 3, 6 in which steric influences are completely absent, the reactions proceeding according to the following scheme:

$$CH_2(C_6H_4\cdot NMe_2)_2 \xrightarrow{CN\cdot Br} CH_2(C_6H_4\cdot NMe_3Br)_2 \text{ and } CH_2(C_6H_4\cdot NMe\cdot CN)_2.$$

$$CH_2(C_6H_4\cdot NMe_2)_2 \xrightarrow{CH_2I\cdot CN} NMe_3I\cdot C_6H_4\cdot CH_2\cdot C_6H_4\cdot NMe\cdot CH_2\cdot CN + CH_2(C_6H_4\cdot NMe\cdot CH_2\cdot CN)_2 \text{ and } CH_2(C_6H_4\cdot NMe_3I)_2$$

That the presence of meta-substituents has little effect on the inter-

action of tertiary amines and cyanogen bromide or iodoacetonitrile has been shown by the behaviour of *m*-chlorodimethylaniline and dimethyl-*m*-toluidine, both of which react with these compounds almost as readily as dimethylaniline and dimethyl-*p*-toluidine.

m-*Tolyltrimethylammonium bromide*, obtained together with m-*tolylmethylcyanamide*, $C_6H_4Me\cdot NMe\cdot CN$, a yellow oil, b. p. 142—144°/8 mm., by the action of cyanogen bromide on dimethyl-*m*-toluidine, volatilises at about 200° without melting.

m-Chlorodimethylaniline and cyanogen bromide give rise to m-*chlorophenylmethylcyanamide*, $C_6H_4Cl\cdot NMe\cdot CN$. This has m. p. 72°, and is readily hydrolysed to *m*-chloromethylaniline, which is thus obtained more readily and in better yield than by the direct methylation of *m*-chloroaniline. Iodoacetonitrile reacts with dimethyl-*m*-toluidine, yielding m-*tolyltrimethylammonium iodide*, m. p. 177°, and *methylcyanomethyl*-m-*toluidine* [N-*methyl*-m-*toluidinoacetonitrile*],

$$C_6H_4Me\cdot NMe\cdot CH_2\cdot CN,$$

a yellow oil, b. p. 158°/8 mm. With *m*-chlorodimethylaniline it yields m-*chlorophenyltrimethylammonium iodide*, m. p. 187°, and *methylcyanomethyl*-m-*chloroaniline* [N-*methyl*-m-*chloroanilinoacetonitrile*],

$$C_6H_4Cl\cdot NMe\cdot CH_2\cdot CN,$$

b. p. 175—180°/9 mm.

4 : 4'-*Tetramethyldiamino*-o : m-*ditolylmethane*,

$$CH_2(C_6H_3Me\cdot NMe_2)_2,$$

prepared by condensing 4-dimethylamino-3-methylbenzyl alcohol with dimethyl-*m*-toluidine in the presence of zinc chloride, is a yellow oil, b. p. 244—246°/10 mm., and readily combines with methyl iodide to form a *dimethiodide*, m. p. 232—234°.

6 : 4'-*Tetramethyldiaminodi*-m-*tolylmethane*, obtained from 2-dimethylamino-5-methylbenzyl alcohol and dimethyl-*o*-toluidine in a similar manner, has b. p. 218—222°/11 mm., yields a *picrate*, m. p. 95°, and forms a *dimethiodide*, lustrous leaflets, m. p. 195°.

4 : 6'-*Tetramethyldiamino*-o : m-*ditolylmethane*, prepared from 2-dimethylamino-5-methylbenzyl alcohol and dimethyl-*m*-toluidine, has b. p. 230—235°/12 mm., and forms a *dimethiodide*, m. p. 209°.

Of the compounds produced by the action of cyanogen bromide and iodoacetonitrile on the 10 amines enumerated above, the following are described: the *dicyano*-compound,

$$CH_2(C_6H_3Me\cdot NMe\cdot CN)_2$$

(lustrous leaflets, m. p. 130°), derived from 6, together with the corresponding *dicyanomethyl* compound,

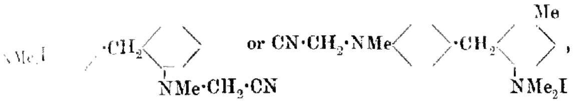
$$CH_2(C_6H_3Me\cdot NMe\cdot CH_2\cdot CN)_2,$$

needles, m. p. 134°, and the *cyanomethyl-methiodide*,

$$NMe_3I\cdot C_6H_3Me\cdot CH_2\cdot C_6H_3Me\cdot NMe\cdot CH_2\cdot CN,$$

lustrous leaflets, m. p. 143°; the *dimethiodide* from 6 has m. p. 243°. The *dicyano*-compound from 3 has m. p. 125°; the *dimethiodide*, m. p. 205°.

The *dicyano*-derivative from 7 forms long needles, m. p. 151°; the *dicyanomethyl* derivative, leaflets, m. p. 104°; the corresponding *cyanomethyl-methiodide*,



... p. 165.

... derivatives formed by the action of iodoacetonitrile on the ... 8 and 10, only the *dimethiodides* and the *dicyanomethyl* ... derived from 8 were isolated.

The action of cyanogen bromide on 5, 8 and 10 yields the corre... *dicyano*-derivatives, which have m. p. 96—97°, 90—91°, and ... (with previous softening at 115°) respectively.

The behaviour of 4:4'-tetramethyldiamino-3-chlorodiphenylmethane and 4:4'-tetramethyldiamino-5-chlorodiphenylmethane towards cyanogen bromide and iodoacetonitrile is similar to that of the analogously constituted methyl compounds 5 and 7. The first-named base yields a *dicyano*-derivative, m. p. 157°; the corresponding *dicyanomethyl* compound and *cyanomethyl-methiodide* have m. p. 105° and 141°. F. B.

Oxonium Compounds. III. GEORGE L. STADNIKOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1391—1414. Compare A., 1912, i, 971).—The greater part of this paper has been already abstracted (this vol., i, 1,833).

The author further shows experimentally that, in the action of 3 mols. of diphenylmethyl ethyl ether on magnesium propyl iodide under the conditions employed by Tschelincev and Pavlov (this vol., i, 461), part of the etherate passes into solution. During distillation, this etherate is subjected to a very high temperature (280°), and it is hence not surprising that it decomposes with formation of tetraphenylethane. Other results obtained by these authors are also criticised.

Gorski's results (this vol., i, 462) are not new (see Oddo, A., 1911, i, 113). T. H. P.

Triphenylthiocarbinol. DANIEL VORLÄNDER and ERNST MITTAG (*Ber.*, 1913, **46**, 3450—3460).—Although triphenylcarbinol contains three phenyl groups its acid properties are no greater than those of an aliphatic alcohol. It has, however, more pronounced basic properties than any other tertiary alcohol, and shows a marked tendency to lose its hydroxyl group.

This behaviour is in accordance with the rules laid down by Vorländer (A., 1902, i, 309), according to which the reactivating influence of unsaturated groups on adjacent atoms or groups attains a maximum in the 3:4-position. The unsaturated phenyl groups in triphenylcarbinol occupy the 3:4-position with respect to the oxygen atom, which, therefore, is very mobile and readily separates from the molecule in the form of hydroxyl: $(\overset{4}{C}{=}\overset{3}{C})\cdot\overset{2}{C}\cdot\overset{1}{O}\cdot H$. In order to ascertain the effect of substituting sulphur in place of oxygen in the above system, the authors have examined the behaviour of triphenylcarbinyl-

mercaptan, and find that, in accordance with the above rule, it shows a marked tendency to rupture between the sulphur and central carbon atoms. Its acid properties are scarcely more pronounced than those of hydrogen sulphide or methyl mercaptan. It dissolves in alkali hydroxides, but the salts thus formed are readily hydrolysed by water. It comparison with other thio-alcohols it shows a marked tendency to lose the thiol group. On treatment with concentrated sulphuric acid or perchloric acid it evolves hydrogen sulphide and is transformed into triphenylcarbinol. A similar decomposition occurs when the thiocarbinol is heated with acetic acid or acetic anhydride. With hydrogen chloride in benzene solution it yields hydrogen sulphide and ω-chlorotriphenylmethane. When boiled with dilute aqueous alkali hydroxides it slowly forms the corresponding alkali sulphides.

The behaviour towards silver salts is very characteristic. It instantly reacts with silver nitrate in alcoholic solution, yielding silver sulphide and triphenylcarbinol; in this respect it resembles the hydrosulphides of the alkali-metals or metals of the alkaline earths. With silver perchlorate in benzene solution it forms silver sulphide and triphenylmethyl perchlorate.

The benzoyl and acetyl derivatives, and also the methyl ether, resemble the parent substance in being readily ruptured between the sulphur and central carbon atoms. Thus, the methyl ether on treatment with alcoholic silver nitrate yields the silver salt of methyl mercaptan, whilst with concentrated sulphuric acid or dilute hydrochloric acid, the mercaptan itself is produced; with alcoholic silver nitrate the benzoyl derivative yields silver thiobenzoate.

The readiness with which triphenylcarbinylmercaptan suffers rupture between the sulphur and central carbon atoms indicates that the union between these atoms is very similar to that between the chlorine and carbon atoms in ω-chlorotriphenylmethane. On the other hand, the union between the cyano-group and central carbon atom in triphenylacetonitrile is much more stable, for this compound does not react with silver nitrate, and is unattacked by sulphuric or perchloric acids.

Attempts to prepare triphenylcarbinyl mercaptan and triphenylacetonitrile by the action of hydrogen sulphide and hydrogen cyanide on triphenylcarbinol were unsuccessful.

By passing hydrogen sulphide into ω-chlorotriphenylmethane at 120—150°, triphenylmethane, sulphur, and hydrogen chloride were produced.

Reduction of the thiocarbinol with sodium and alcohol yields triphenylmethane and sodium sulphide, whilst the action of chlorine in carbon tetrachloride solution gives rise to ω-chlorotriphenylmethane.

The behaviour of triphenylmethyl disulphide, $(CPh_3)_2S_2$, has also been investigated. On treatment with perchloric acid it liberates hydrogen sulphide, but not so readily as the thiocarbinol. It is transformed by chlorine into ω-chlorotriphenylmethane.

Triphenylcarbinyl mercaptan [*ω-thioltriphenylmethane*], $CPh_3\cdot SH$, prepared by saturating a solution of sodium ethoxide in ethyl alcohol with hydrogen sulphide and heating the resulting solution of sodium

the sulphide with ω-chlorotriphenylmethane, separates from alcohol in long, white, prismatic crystals, m. p. 107°. The *sodium* salt is obtained by shaking an ethereal solution of the thiocarbinol with concentrated aqueous potassium hydroxide. The *lead* and *mercuric* salts are also described.

The acetyl and benzoyl derivatives, prepared by the action of the acid chlorides on the carbinol in pyridine solution, have m. p. 139—141° and 185° respectively, and are decomposed by sulphuric acid with the evolution of hydrogen sulphide (compare Wheeler, A., 1902, i, 28; Meyer and Fischer, 1911, i, 120).

Triphenylmethyl disulphide is obtained in colourless needles by the addition of sulphuryl chloride to an ice-cold, alcoholic solution of the sodium salt of the thiocarbinol; it becomes yellow, and begins to decompose at 140°, m. p. about 155°.

Triphenylmethyl methyl sulphide, prepared by the action of methyl sulphate on a solution of the thiocarbinol in methyl-alcoholic sodium methoxide, or by heating the carbinol with methyl iodide and potassium hydroxide in methyl-alcoholic solution, has m. p. 105—106° (compare Meyer and Fischer, *loc. cit.*). F. B.

Action of Dimethylamine on the Iodohydrins of Styrene; Study of the Two Phenyldimethylaminoethanols. MARC TIFFENEAU and ERNEST FOURNEAU (*Bull. Soc. chim.*, 1913, [iv], **13**, 971—981).—The authors have confirmed Krassusky's views that the formation of an amino-alcohol from a chloro- or iodo-hydrin takes place through the intermediate formation of an ethylene oxide (compare A., 1908, i, 139). The two isomeric styrene iodohydrins, $OH·CHPh·CH_2I$ and $CHPhI·CH_2·OH$, both react with dimethylamine to give the same β-dimethylamino-α-phenylethanol, $OH·CHPh·CH_2·NMe_2$, which is also obtained by the interaction of styrene oxide and dimethylamine. It is a liquid, b. p. 132—133°/15 mm., D_4^0 1·021 (compare Tiffeneau, *Ann. Chim. Phys.*, 1907, [viii], **10**, 342). It yields a *hydrochloride*, m. p. 147°; a *picrate*, m. p. 35—40°; a benzoyl hydrochloride, m. p. 210° (compare *loc. cit.*); a *morpholone hydrochloride*, m. p. 229°, from interaction in benzene solution with ethyl chloroacetate; a *methiodide*, m. p. 225°; a *methochloride*, m. p. 199—200°, by the action of silver chloride on the methiodide. This methochloride, which is the hydrochloride of secondary phenylcholine, gives an *aurichloride*, m. p. 154°, soluble in water, and a *picrate*, prismatic needles, m. p. 195°.

Styrene methyliodohydrin reacts similarly with dimethylamine, yielding *β-dimethylamino-α-methoxy-α-phenylethane*, $OMe·CHPh·CH_2·NMe_2$, b. p. 105—107°/15 mm., 229—230°/760 mm.; D_4^0 1·0013, which gives a *hydrochloride*, m. p. 228°; a *hydriodide*, m. p. 205°, and a *methiodide*, m. p. 180°. Styrene ethyliodohydrin similarly yields *β-dimethylamino-α-ethoxy-α-phenylethane*, b. p. 118—119°/19 mm., 229—230°/760 mm., D_4^0 0·9623, giving a *hydrochloride*, m. p. 134°, a *hydriodide*, m. p. 153°, and a *methiodide*, m. p. 157°.

In further proof that the styrene iodohydrin, $CHPhI·CH_2·OH$, does not yield the corresponding dimethylaminoethanol,

$$NMe_2·CHPh·CH_2·OH,$$

but the isomeric ethanol, the former has been prepared by other methods and characterised as follows:

Phenylacetyl chloride was brominated by direct addition of bromine to the acid chloride at 80°, the product being finally boiled with excess of alcohol, giving *ethyl α-bromophenylacetate*, b. p. 145°/15 mm. This substance reacts with dimethylamine in benzene solution to give *ethyl α-dimethylaminophenylacetate*, $NMe_2\cdot CHPh\cdot CO_2Et$, b. p. 135°/13 mm., which is readily reduced by sodium in absolute alcohol to *α-dimethylamino-α-phenylethanol*, $NMe_2\cdot CHPh\cdot CH_2\cdot OH$, b. p. 135—138°/15 mm. and 248—250°/760 mm., solidifying at −5°. The following derivatives have been prepared: *hydrochloride*, m. p. 114°; *picrate*, m. p. 115°; *gold* salt, m. p. 110°, decomposed on boiling with water, reduced gold being deposited; *benzoyl* derivative, m. p. 165°; *morpholine hydrochloride*, m. p. 220°, sparingly soluble in alcohol; *methiodide*, difficult to crystallise; *methochloride* [primary *phenylcholine hydrochloride*], $NMe_3Cl\cdot CHPh\cdot CH_2\cdot OH$, yielding a crystalline *gold* salt and a *picrate*, m. p. 165°. W. G.

Electrolysis in Non-Aqueous Solvents. *o*-Nitrobenzoic Acid Solutions of Potassium *o*-Nitrobenzoate. CARL SCHALL (*Zeitsch. Elektrochem.*, 1913, **19**, 830—833).—Berl (A., 1904, i, 282) showed that the electrolysis of fused organic salts led to results which differed from those obtained from the electrolysis of aqueous solutions of these salts. In the case of the sodium salt of *o*-nitrobenzoic acid melted with its free acid, the product was nitrobenzene, and not 2 : 2′-dinitrodiphenyl as was expected. The author has electrolysed a 15% solution of potassium *o*-nitrobenzoate in *o*-nitrobenzoic acid at 160—170°, using a small porous pot as anode vessel and a beaker as cathode vessel. The anode consisted of 6—7 cms. of platinum wire wound into a spiral, and the cathode was a platinum foil 3 cms. × 7 cms. The electrolysis was carried out by a current of 5 amperes and 50 volts. During the electrolysis an odour of aniline was noticed. On allowing the fusion to cool, the cathode material contained a small quantity of a liquid with an *iso*nitrile odour, and a black substance which dissolved in alkali and acid. The anode vessel contained a little *o*-nitrophenol, a little 2 : 2′-dinitrodiphenyl, and a brown powder of undetermined composition. The experiment of Lilienfeld (D.R.-P. 1902, 147943) was repeated; by this 2 : 2′-dinitrodiphenyl should be obtained by the electrolysis of copper *o*-nitrobenzoate in aqueous solution. The author is unable to obtain any of this compound either under the specified or any other conditions. J. F. S.

Nitro-*o*-sulphobenzoic Acid and Some of its Derivatives. MARTIN BELL STUBBS (*Amer. Chem. J.*, 1913, **50**, 193—204. Compare Taverne, A., 1906, i, 273).—If *o*-sulphobenzoic acid is treated with a mixture of fuming nitric and concentrated sulphuric acids, the mixture heated until all the nitric acid has been eliminated, and water added to the cooled product, *5-nitro-2-sulphobenzoic anhydride*,

$$NO_2\cdot C_6H_3{<}{\genfrac{}{}{0pt}{}{SO_2}{CO}}{>}O,$$

m. p. about 212° (uncorr.), separates in white crystals. *Potassium*

[illegible] *5-nitro-2-sulphobenzoate* crystallises with $1H_2O$, the *lead* salt with $2H_2O$, the *barium* salt with $3H_2O$, and the *copper* salt with $2H_2O$, the *calcium* salt also contains water of crystallisation, whilst the *potassium* salt is anhydrous. On treating the *chloride*,

$$NO_2\cdot C_6H_3(SO_2Cl)\cdot COCl,$$

a yellow oil, with dry ammonia, the *sulphinide*,

$$NO_2\cdot C_6H_3<{SO_2 \atop CO}>NH,$$

[illegible]; its *sodium* salt crystallises with $1H_2O$. When the *ethyl ester* of the *chloride*, $NO_2\cdot C_6H_3(SO_2Cl)\cdot CO_2Et$, obtained as an oil by the action of alcohol on the chloride, is neutralised with barium carbonate, *barium ethyl 5-nitro-2-sulphobenzoate*,

$$[NO_2\cdot C_6H_3(CO_2Et)\cdot SO_3]_2Ba,3H_2O,$$

is produced, which forms colourless needles. E. G.

Characterisation of 3 : 5-Dibromotyrosine. CARL TH. MÖRNER (*Zeitsch. physiol. Chem.*, 1913, **88**, 124—137).—In view of its importance as a product of hydrolysis of a natural protein (gorgonin), 3 : 5-dibromotyrosine has been studied in detail.

Dibromo-*l*-tyrosine crystallises anhydrous in long, slender needles grouped in voluminous bundles or balls, or with $2H_2O$ in thin plates similar to benzoic acid. It has $[\alpha]_D^{20}$ $+1\cdot3°$.

Dibromo-*dl*-tyrosine crystallises $+H_2O$ in transparent, four-edged prisms or thick plates. It is nearly twice as soluble in water as the isomeride. Both forms have m. p. about 245° (much decomp.). They are stable to concentrated sulphuric and hydrochloric acids even on heating. The bromine atoms are removed quantitatively on heating with zinc dust. E. F. A.

Ketens. XXIV. Mixed Diphenylacetic Anhydrides and their Decomposition. HERMANN STAUDINGER, E. ANTHES, and H. SCHNEIDER (*Ber.*, 1913, **46**, 3539—3551).—It has been previously shown (Staudinger and Ott, A., 1908, i, 602) that anhydrides of malonic acid decompose when heated, yielding carbon dioxide and ketens. The scope of this method of preparation is greatly limited by the difficulty of preparing such anhydrides, and the authors have therefore investigated the behaviour of mixed anhydrides of malonic and other acids (compare Staudinger and Bereza, A., 1909, i, 83) which can be readily prepared by the action of ketens on malonic acid.

The authors have prepared a series of mixed anhydrides by the action of diphenylketen on derivatives of malonic acid. These are stable, well-crystallised substances which appear to be unimolecular, and thus differ remarkably from the amorphous, polymerised dimethyl- and diethyl-malonic anhydrides (A., 1908, i, 939). An anhydride could not, however, be obtained from malonic acid itself, decomposition occurring in this case at a low temperature with formation of diphenylacetic anhydride and brown, resinous products.

The action of heat on the mixed anhydrides causes a primary dissociation into diphenylacetic anhydride and the corresponding malonic anhydride; the latter then loses carbon dioxide to yield the keten. Dimethylketen and diethylketen can be obtained in this

manner from dimethyl- and diethyl-malonic diphenylacetic anhydride, respectively. In the latter case, however, small quantities of diphenylketen are also produced. This is attributed to the partial decomposition of diphenylacetic anhydride into diphenylketen and diphenylacetic acid, the latter substance also uniting with a portion of the diethylketen and thus reducing the yield of the latter. A similar secondary decomposition occurs quantitatively during the decomposition of benzylidenemalonic diphenylacetic anhydride, so that the product of the reaction is diphenylketen instead of the expected benzylideneketen, whilst the desired ketens were also not obtained from *iso*propylidenemalonic diphenylacetic anhydride and dichloromalonic diphenylacetic anhydride. Ethylchloroketen, on the other hand, was readily obtained from ethylchloromalonic diphenylacetic anhydride.

The mixed anhydrides are prepared by the addition of diphenylketen to very concentrated solution or suspension of the malonic acid in absolute ether, reaction being allowed to proceed in an atmosphere of carbon dioxide. After a period which depends on the derivative of malonic acid employed, the mixed anhydride separates in the crystalline state. The m. p.'s of the products depend somewhat on the manner of heating.

Dimethylmalonic diphenylacetic anhydride, $CMe_2(CO{\cdot}O{\cdot}CO{\cdot}CHPh_2)_2$, has m. p. 91° (decomp.). When heated at the ordinary pressure, it yields only small quantities of dimethylketen; when decomposed in a vacuum, however, the yield of the latter amounts to 50%. The liquid polymeric compound (Staudinger and Klever, A., 1907, i, 424) of dimethylketen appears to be formed in small quantity, whilst the residue consists of almost pure diphenylacetic anhydride.

Diethylmalonic diphenylacetic anhydride, m. p. 94°, when heated in a vacuum gives a 64% yield of diethylketen; at a somewhat higher temperature, diphenylketen is evolved, which is identified by conversion into diphenylacetanilide.

Diphenylacetic anhydride is obtained by the action of diphenylketen on an ethereal solution of ethylmalonic acid. The products of the decomposition of ethylmalonic anhydride have not yet been investigated.

Benzylidenemalonic diphenylacetic anhydride, m. p. 103°, is more stable than the preceding compounds. When heated to 180° in a vacuum, it yields diphenylketen. Cinnamic and diphenylacetic acids are obtained by saponification of the residue from the distillation.

iso*Propylidenemalonic diphenylacetic anhydride*, m. p. 101°, decomposes slowly at its melting point. When distilled in a vacuum it yields diphenylketen; the residue consists of dark brown, pasty mass, which is probably formed by the rapid polymerisation of the keten and subsequent decomposition of the polymerisation product.

Dichloromalonic diphenylacetic anhydride, m. p. 74° (decomp.), is an unstable substance, which slowly decomposes at the ordinary temperature. When heated, it yields more than the calculated quantity of carbon dioxide, and, at a higher temperature, evolves hydrogen chloride. Dichloroketen has not been isolated.

Ethylchloromalonic acid, m. p. 101—102°, is obtained by boiling an absolute ethereal solution of ethylmalonic acid with sulphuryl chloride

compare Conrad and Reinbach, A., 1902, i, 529). It combines with diphenylketen, yielding *ethylchloromalonic diphenylacetic anhydride*, m. p. 95—96°, which, when heated in a vacuum, gives *ethylchloroketen*, $CEtCl:CO$. The latter condenses at $-80°$ to yellow oily drops which in a few minutes, become transformed into a white solid mass. Attempts to obtain the unpolymerised keten at $-180°$ were unsuccessful. In ethereal solutions at $-80°$, it can only be preserved for a short time. The keten vapours dissolve in other with a yellow colour, but, after a few seconds, the solution becomes colourless and, on removal of ether, the keten remains as a glassy, somewhat viscous mass, which is no longer completely soluble in the solvent. The keten polymeride is soluble in carbon disulphide, and melts indefinitely at 74—80°. When heated, it decomposes completely, evolving hydrogen chloride and probably chlorobutyryl chloride.

Ethylchloroketen unites with aniline to form chlorobutyranilide.

H. W.

Conversion of Triphenylmethyl into Triphenylacetic Acid.

ALEXANDER I. GORSKI (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 1454—1460). —In consequence of the varying behaviour of heated and non-heated ethereal solutions of magnesium triphenylmethyl chloride towards aromatic aldehydes, Schmidlin (A., 1906, i, 392; 1907, i, 26, 601; 1908, i, 239; this vol., i, 50) assumes the existence of two isomeric organo-magnesium compounds of ω-chlorotriphenylmethane: a normal, stable β-compound, which gives β-benzopinacolin with benzaldehyde, and an unstable quinonoid α-compound, which gives *p*-benzoyltriphenylmethane.

Tschitschibabin (A., 1907, i, 1022) is, however, of the opinion that only one such organo-magnesium compound exists.

Since the experimental results given by Schmidlin in support of his assumption were not obtained under the conditions in which tho conversion of the α- into the β-compound actually occurs, the author has investigated the reaction further. By passing dry carbon dioxide into a heated mixture of a benzene solution of triphenylmethyl and the etherate of magnesium iodide, he has succeeded in obtaining good yields of triphenylacetic acid and triphenylmethane; decomposition of the products by means of water failed to give any appreciable amount of triphenylmethyl peroxide. This result is regarded as evidence in favour of Tschitschibabin's view that Schmidlin's α-compound is really a mixture of an ethereal solution of triphenylmethyl with the etherate of magnesium chloride.

T. H. P.

α-*p*-Nitrophenyl-β-hydroxythionaphthen.

HERMANN APITZSCH (*Ber.*, 1913, 46, 3091—3103. Compare A., 1909, i, 46).—p-*Nitrobenzylthiosalicylic acid* [2-p-*nitrobenzylthiolbenzoic acid*],

$$NO_2\cdot C_6H_4\cdot CH_2\cdot S\cdot C_6H_4\cdot CO_2H,$$

practically colourless, shining prisms, m. p. 215·5° (corr.) after softening at 200°, is prepared by the addition of an alcoholic solution of *p*-nitrobenzyl chloride to an aqueous alcoholic solution of sodium thiosalicylate [*o*-thiolbenzoate] and acidification of the mixture with hydrochloric acid. It dissolves in alkali to a pure yellow solution,

which becomes dark reddish-brown on warming, and from which a definite compound could not be isolated. Small quantities of p-*nitrobenzyl* 2-p-*nitrobenzylthiolbenzoate*,

$$NO_2\cdot C_6H_4\cdot CH_2\cdot S\cdot C_6H_4\cdot CO\cdot O\cdot CH_2\cdot C_6H_4\cdot NO_2,$$

pale yellow crystals, m. p. 194°, are obtained as by-product in the preparation of the acid. Methyl alcohol and hydrochloric acid transform the acid into its *methyl* ester, m. p. 111—112°, which is also obtained by the action of *p*-nitrobenzyl chloride on methyl thiolsalicylate in methyl alcoholic solution in the presence of the calculated amount of 2*N*-potassium hydroxide. When boiled with a methyl alcoholic solution of sodium methoxide and subsequently carefully acidified with acetic acid, the methyl ester is converted into 2-*hydroxy*-1-p-*nitrophenylthionaphthen*, $C_6H_4{<}{\overset{C(OH)}{\underset{S}{}}}{>}C\cdot C_6H_4\cdot NO_2$, which exists in a yellow ketonic form, a red enolic form, and as an orange-red mixture. The forms readily pass into one another, so that definite directions for the productions of a definite modification cannot readily be given.. The red form, however, which decomposes at 195° after previous softening, is obtained when this crude product is crystallised from aqueous alcohol. From ethyl acetate, chloroform, or glacial acetic acid solution, the yellow keto-form frequently separates in well defined, rhombohedric crystals, usually mixed with the red needles. The mixed form is obtained from solutions of the crude product in benzene, toluene, or xylene in the form of thin, orange-red needles, which are stable and do not become yellow on drying.

In the following experiments the red modification was used. When treated with an equivalent quantity of sodium methoxide in absolute alcoholic solution, the *sodium* salt, $C_{14}H_8O_3NSNa$, blue needles, is obtained. Benzyl chloride in the presence of alkali in aqueous alcoholic or absolute alcoholic solution yields two *benzyl* derivatives, greenish-yellow needles, m. p. 143·5° after softening at 142°, and almost colourless, irregularly formed needles, m. p. 144—145° (corr.), which can be separated by crystallisation from alcohol. A mixture of the two forms melts at 120°. Treatment with ethyl bromide leads to the formation of only one *ethyl* derivative, yellow needles, m. p. 109·5°.

2-*Hydroxy*-1-p-*aminophenylthionaphthen*,

$$C_6H_4{<}{\overset{C(OH)}{\underset{S}{}}}{>}C\cdot C_6H_4\cdot NH_2,$$

is obtained by the reduction of an alkaline, aqueous alcoholic solution of the nitro-compound by sodium hyposulphite. The substance is purified with difficulty, since it is readily decomposed when warmed in indifferent solvents. It forms white needles, m. p. 130° (corr.), which are sensitive to the action of light and air. The *picrate*, brown needles, begins to decompose at 165°. The salts with mineral acids are generally sparingly soluble and decompose readily. The *oxalate* is converted by nitric acid into a diazonium salt, which couples with R-salt in alkaline solution.

o-Benzylthiolbenzoic acid, needles, m. p. 189°, is formed from benzyl chloride, thiosalicylic acid, and potassium carbonate in boiling aqueous alcoholic solution.

Methyl 2-o-nitrobenzylthiolbenzoate, m. p. 122·5° (corr.), and *methyl 2-m-nitrobenzylthiolbenzoate*, rhombohedric plates, m. p. 88—89° (corr.), are obtained from methyl thiosalicylate, 2*N*-potassium hydroxide, and the requisite nitrobenzyl chloride. They resemble the non-nitrated benzylthiosalicylic acid, in that they do not yield a condensation product when boiled with aqueous alcoholic alkali. H. W.

Vinylphthalimide. MARCEL BACHSTEZ (*Ber.*, 1913, **46**, 3087—3089).—Since phthalylglycyl chloride decomposes when heated into carbon monoxide and chloromethylphthalimide (Gabriel, A., 1908, i, 181), whilst *a*-phthaliminoisobutyryl chloride decomposes according to the scheme:

$$C_8H_4O_2{:}N\cdot CMe_2\cdot COCl \rightarrow CO + HCl + C_8H_4O_2{:}N\cdot CMe{:}CH_2$$

(Gabriel, A., 1911, i, 982), the author has examined the action of heat on *a*-phthalylalanyl chloride (A., 1908, i, 182), and has thereby obtained small quantities of *vinylphthalimide*,

$$C_8H_4O_2{:}N\cdot CH{:}CH_2,$$

rhombic plates, m. p. 86°. Attempts to improve the yield by the addition of traces of zinc chloride or aluminium chloride were unsuccessful. The substance unites with bromine to form *phthalimino-αβ-dibromoethane*, needles, m. p. 123—124°, which rapidly decomposes when preserved in the presence of moisture.

A further attempt was made to prepare vinylphthalimide by the abstraction of hydrobromic acid from β-bromoethylphthalimide (compare Johnson and Jones, A., 1911, i, 455) by the action of sodium phenoxide in alcoholic solution. Phenoxyethylphthalimide, m. p. 129—130° (Schmidt, A., 1890, 372), was thereby obtained.

Small quantities of vinylphthalimide were obtained by the action of phosphoric oxide on β-hydroxyethylphthalimide (compare Gabriel, A., 1905, i, 265). H. W.

Toad Venom. HEINRICH WIELAND and FRIEDRICH JOS. WEIL (*Ber.*, 1913, **46**, 3315—3327).—Bufotalin, the poisonous principle of the toad first isolated in an amorphous condition by Faust (A., 1902, i, 446), has now been obtained in the crystalline state. It has the composition $C_{16}H_{24}O_4$, is faintly dextrorotatory and neutral in character. Alkali converts it into the unsaturated bufotalic acid, proving bufotalin to be a lactone. The other two oxygen atoms are present as alcoholic hydroxyl groups. Concentrated hydrogen chloride in the cold eliminates two molecules of water, forming a pale yellow, crystalline compound, $C_{16}H_{20}O_2$, bufotalien. It takes up two atoms of hydrogen in presence of palladium black.

Acetyl chloride in pyridine or warming with acetic anhydride converts bufotalin into a doubly acetylated ether, one hydroxyl group in each molecule being acetylated and the two molecules united through oxygen. Treatment of this diacetyl ether with concentrated hydrochloric acid forms a yellow, strongly unsaturated compound, $C_{18}H_{22}O_3$. The same compound is obtained on heating bufotalein with acetic anhydride, which effects direct acetylation on the carbon. Acetic anhydride is added directly to the C:C complex from which acetic acid is subsequently eliminated.

During the conversion of diacetylbufotalin ether into acetylbufotalin, the bridge oxygen is first eliminated as water. The single molecules, $-C(OAc):CH-$, undergo rearrangement to a saturated diketone, $-CO\cdot CHAc-$, which loses water to form the doubly unsaturated monoketone, $-CH:CH\cdot CH:CAc-$. The analogy between bufotalin, $C_{15}H_{22}(OH)_3\cdot CO_2H$, and cholic acid, $C_{22}H_{36}(OH)_3\cdot CO_2H$, is emphasised. The unsaturated derivatives of both groups give Liebermann's characteristic cholestol reaction with acetic anhydride and sulphuric acid.

Bufotalin is not identical with bufagin, $C_{18}H_{24}O_4$, obtained from the tropical toad by Abel and Macht (A., 1912, ii, 1193).

Bufotalin has m. p. 148° (decomp.), $[\alpha]_D^{20} + 5\cdot 4°$; it dissolves in concentrated sulphuric acid with an orange-red coloration which becomes deep red on standing and shows a green fluorescence.

Bufotalien forms pale yellow platelets, m. p. 219°. *Acetylbufotalien* separates in lustrous, yellow platelets grouped in rosettes, m. p. 1[illegible] (decomp.). *Diacetylbufotalin ether* forms colourless, lustrous platelets, m. p. 254° to a red liquid. E. F. A.

Action of Chloroacetic Acid on Phenolcarboxylic Acids and Nitrophenols. Richard Meyer and Casimir Duczmal (*Ber.*, 1913, **46**, 3366—3379).—Although the reaction of chloroacetic acid with alcohols and phenols producing ethers according to the equation $R\cdot OH + CH_2Cl\cdot CO_2H = HCl + OR\cdot CH_2\cdot CO_2H$ is a fairly general one, it is usually understood that this reaction fails with salicylic acid. The authors find that the reaction can be effected with salicylic acid, although less readily than with most other substances, and, indeed, mere mention of this fact has already appeared (Bogisch, *Diss.*, Stuttgart, 1889), although it has not found its place in the usual literature. The behaviour of the isomeric hydroxybenzoic acids and of the nitrophenols towards chloroacetic acid is also investigated.

The most satisfactory procedure for the reaction with salicylic acid is to dissolve equimolecular quantities of this substance and chloroacetic acid in a concentrated solution of a termolecular quantity of sodium hydroxide. The sodium salt of *o*-carboxyphenoxyacetic acid separates, and the reaction can be completed by heating for some hours on a water-bath. Any salicylic acid in the liberated acid product can be removed by extraction with ether. The yield of *o*-carboxyphenoxyacetic acid, $CO_2H\cdot C_6H_4\cdot O\cdot CH_2\cdot CO_2H$, m. p. 190—192°, calculated on the salicylic acid consumed amounts to approximately 80%.

m-Hydroxybenzoic acid, dissolved in sodium hydroxide solution of 35% strength, when gradually treated with chloroacetic acid gave rise to *m*-carboxyphenoxyacetic acid, m. p. 206—207°.

When equimolecular quantities of ethyl chloroacetate and sodium *m*-hydroxybenzoate are heated together in a sealed tube at 170° for thirty hours, *ethyl* m-*hydroxybenzoyloxyacetate* is obtained as a viscous oil, which can be hydrolysed by sodium hydroxide solution at 3° to m-*hydroxybenzoyloxyacetic acid*,

$$CO_2H\cdot CH_2\cdot O\cdot CO\cdot C_6H_4\cdot OH,$$

prisms, m. p. 138—140°. On warming with sodium hydroxide solution it is hydrolysed to *m*-hydroxybenzoic acid.

When treated in boiling sodium hydroxide solution (35%) with an equimolecular quantity of chloroacetic acid, *p*-hydroxybenzoic acid is converted into *p*-carboxyphenoxyacetic acid, m. p. 278°.

The action of ethyl chloroacetate on sodium *p*-hydroxybenzoate is similar to the meta-compound and requires similar conditions; the product is an oily *ethyl* ester, which on hydrolysis with cooled sodium hydroxide solution yields p-*hydroxybenzoyloxyacetic acid*,

$$CO_2H\cdot CH_2\cdot O\cdot CO\cdot C_6H_4\cdot OH,$$

silky needles, m. p. 174—175°.

o-Cresotic acid when treated in sodium hydroxide solution with chloroacetic acid produces 3-*carboxy*-o-*tolyloxyacetic acid*, needles, m. p. 203—204°. In a similar manner, *m*-cresotic acid gives rise to 4-*carboxy*-m-*tolyloxyacetic acid*, nodular aggregates, m. p. 164—165°, whilst the *p*-cresotic acid yields 3-*carboxy*-p-*tolyloxyacetic acid*, leaflets, m. p. 185°.

1:2- and 2:3-Hydroxynaphthoic acids were likewise applied to this synthetic reaction, sufficient sodium hydroxide being used to just neutralise the acid reagents. The former acid gave rise to 2-*carboxy*-1-*naphthoxyacetic acid*, silky needles, m. p. 206—207°, whilst the 2:3-isomeride produced 3-*carboxy*-2-*naphthoxyacetic acid*, leaflets, m. p. 224—225°.

Chloroacetic acid acts quite normally on the sodium salt of 2:4-dinitrophenol, but as the product is rather unstable, excess of alkali must be avoided; the resulting 2:4-dinitrophenoxyacetic acid had m. p. 147—148°.

No success attended attempts to obtain a condensation product of chloroacetic acid with picric acid, even when the latter was applied as the silver salt; as free picric acid and silver chloride were produced, it is probable that the primary product underwent immediate decomposition.

In all the above cases especial attention was given to the yields of the products, and although the interaction of *o*- and *p*-nitrophenols with chloroacetic acid had already been investigated, experiments were performed to determine the yields; *m*-nitrophenol was found to behave similarly to the others, producing 3-*nitrophenoxyacetic acid*, needles, m. p. 154—155°.

None of the above substances gives a quantitative result; it is found that the ortho-compounds give by far the poorest yields, and the difficulty of reaction observed with salicylic acid is evidently to be attributed to its ortho-configuration. With the meta- and para-compounds the yields are much better, the para-compounds being the more satisfactory.

D. F. T.

The Condensation Product of Methyl 2:3-Hydroxynaphthoate with Benzaldehyde. LEO ROSLAV (*Monatsh.*, 1913, 34, 1503—1518. Compare Friedl, A., 1910, i, 741; also the three following abstracts).—As Friedl has already shown, the chlorine atom of methyl 1-α-chlorobenzyl-2-naphthol-3-carboxylate, the product obtained when hydrogen chloride is passed into a cold mixture of the above

substances, is highly reactive. Many reactions are now described in which this property is exemplified.

On condensation in presence of sodium in benzene, the compound yielded *methyl αβ-diphenylethane-αβ-bis-2-naphthol-3-carboxylate*,

$$C_2H_2Ph_2[C_{10}H_5(OH)\cdot CO_2Me]_2,$$

in microscopic prisms, m. p. 227°, which gave violet-red solutions in sulphuric acid. When boiled with *p*-cresol in benzene, it formed *methyl* 1-α-p-*tolyloxybenzyl-2-naphthol-3-carboxylate*,

$$C_6H_4Me\cdot O\cdot CHPh\cdot C_{10}H_5(OH)\cdot CO_2Me,$$

in microscopic leaflets, m. p. 192—193°, whilst thymol yielded *methyl* 1-α-*thymoxybenzyl-2-naphthol-3-carboxylate*, in yellow, microscopic, rhombic leaflets, m. p. 187—188°.

The chlorine atom in the benzyl group was also replaced by bases, and the following compounds were obtained: from *p*-aminoazobenzene, the α-*benzeneazoanilino*-derivative, slender, orange-yellow needles, m. p. 221°; from carbamide, the α-*carbamido*-derivative, only one amino-group reacting, small, faintly yellow prisms, m. p. 194—195°; from benzylamine, the α-*benzylamino*-derivative, long, rectangular plates, m. p. 105—106°, *hydrochloride*, m. p. 172° (decomp.); from piperidine, the α-*piperidino*-derivative, greenish-yellow, m. p. 145—146°, unstable *hydrochloride*, m. p. 174—175°; from phenylhydrazine, the α-*phenylhydrazino*-derivative, lemon-yellow, hard rosettes, m. p. 188°; from ethyl sodiomalonate, the mixed *ester*,

$$CH(CO_2Et)_2\cdot CHPh\cdot C_{10}H_5(OH)\cdot CO_2Me,$$

long, yellow prisms, m. p. 130—131°.

It was expected that with pyridine the substance might react in its ketonic form and yield an *o*-quinone, but a *pyridinium chloride*, $C_5H_5NCl\cdot CHPh\cdot C_{10}H_5(OH)\cdot CO_2Me$, was precipitated as a yellow powder, decomp. 162—163°, when the base was added to a solution of the compound in benzene. The aqueous solution, especially with silver oxide, soon deposited methyl 1-α-hydroxy-benzyl-2-naphthol-3-carboxylate (Friedl, *loc. cit.*), and potassium hydroxide gave, in addition, the above ethane derivative. Quinoline behaved similarly, but no pure product could be isolated.

Colour reactions with ferric and stannic chlorides, sulphuric and perchloric acids are described. J. C. W.

Condensation of *p*-Tolualdehyde with Methyl 2:3-Hydroxynaphthoate. MARIUS REBEK (*Monatsh.*, 1913, **34**, 1519—1526).—Methyl 2 : 3-hydroxynaphthoate, which, with the ethyl ester, has been crystallographically examined by von Lang, condenses just as readily with *p*-tolualdehyde under the influence of hydrogen chloride or bromide as it does with benzaldehyde. *Methyl* 1-α-*chloro*-p-*methylbenzyl-2-naphthol-3-carboxylate*, $C_6H_4Me\cdot CHCl\cdot C_{10}H_5(OH)\cdot CO_2Me$, forms pale yellow, microscopic tablets, m. p. 143—145°, which give various colour reactions with sulphuric and perchloric acids and stannic and ferric chlorides. The α-*bromo*-derivative forms yellow, glittering, flat leaflets, m. p. 157—159°. In the case of hydrogen bromide, a good yield of the condensation product was obtained when molecular quantities of the reacting substances were diluted with ether. From such a solution, hydrogen chloride gave no crystals for some days.

which, finally, a condensation product of the α-chloro-derivative with same ester, namely, *methyl* p-*xylylidenebis-2-naphthol-3-carboxylate* (p-*tolyldi-2-hydroxy-3-carbomethoxynaphthylmethane*),

$$C_6H_4Me\cdot CH[C_{10}H_5(OH)\cdot CO_2Me]_2,$$

was obtained in well-defined prisms, m. p. 218—222°, which crystallised with ½ mol. of chloroform.

On adding water to a cold acetone solution of the α-bromo-derivative, *methyl* 1-α-*hydroxy*-p-*methylbenzyl-2-naphthol-3-carboxylate*,

$$C_6H_4Me\cdot CH(OH)\cdot C_{10}H_5(OH)\cdot CO_2Me,$$

crystallises in yellow, rhombic leaflets, m. p. 155—158°. This compound tends to condense to an ether, especially in presence of alcohol or hydrochloric acid, or on melting. When the α-chloro-derivative was boiled with moderately strong hydrochloric acid, the same compound, *methyl* αα′-*oxidobis*-1-p-*methylbenzyl-2-naphthol-3-carboxylate*,

$$O[CH(C_6H_4Me)\cdot C_{10}H_5(OH)\cdot CO_2Me]_2,$$

was obtained in yellow, micro-leaflets, m. p. 216·5—219°. The speed of the action with water was roughly determined at ordinary temperatures.

When warmed with acetic anhydride and sodium acetate, the yellow halogen compounds became colourless, and an amorphous, acetylated derivative, which could not be crystallised, was obtained. Methyl alcohol condensed with the compounds to form *methyl* 1-α-*methoxy*-p-*methylbenzyl-2-naphthol-3-carboxylate*,

$$C_6H_4Me\cdot CH(OMe)\cdot C_{10}H_5(OH)\cdot CO_2Me,$$

in microscopic prisms, m. p. 178—180·5°. The α-halogen atom in the xylyl group was also replaced by a number of alcohol- and basic radicles, and the following corresponding condensation products obtained: α-*ethoxy*-derivative, stout, microscopic prisms, m. p. 95—97·5°; α-*propoxy*-derivative, yellow, microscopic prisms, m. p. 105·5—108·5°; α-*phenoxy*-derivative, faintly yellow prisms, m. p. 175—176°; p-*tolyloxy*-derivative, rectangular plates or leaflets, m. p. 165·5—167°; α-*thymoxy*-derivative, stout, microscopic needles, m. p. 188—189°; α-*anilino*-derivative, pale yellow, m. p. 210—211·5°; α-*phenylhydrazino*-derivative, lemon-yellow needles, decomp. 140°; α-*piperidino*-derivative, silky needles, m. p. 172—173·5°; p-*benzeneazoanilino*-derivative, orange, short prisms, m. p. 210—210·5°, reddened by hydrochloric acid vapours.

Methyl α-chloro-1-*p*-methylbenzyl-2-naphthol-3-carboxylate was hydrolysed by adding hydriodic acid to a warm solution in acetic anhydride. p-*Methylbenzyl-2-naphthol-3-carboxylic acid*,

$$C_6H_4Me\cdot CH_2\cdot C_{10}H_5(OH)\cdot CO_2H,$$

formed intensely yellow crystals, m. p. 249—250° (decomp.), and gave a white *silver* salt, decomp. 210°, from which the *methyl* ester, m. p. 137—138°, was prepared. The latter was also present in the product from the above hydrolysis.

Characteristic colour reactions are exhibited by all these compounds.

J. C. W.

Condensation of Anisaldehyde with Methyl 2 : 3-Hydroxynaphthoate. FRITZ WEISHUT (*Monatsh.*, 1913, 34, 1547—1565).—Studies analogous to the foregoing were carried out with anisaldehyde.

Methyl 1-*α-chloro*-p-*methoxybenzyl-2-naphthol-3-carboxylate*,

$OMe\cdot C_6H_4\cdot CHCl\cdot C_{10}H_5(OH)\cdot CO_2Me$,

formed yellow prisms, m. p. 171—173°, decomp. 185°, and gave a series of remarkable colour reactions with strong acids, due to the presence of a carbonium valence. Silver sulphate rendered a warm benzene solution violet-red; the colour disappeared on cooling and returned on warming. The *bromo*-analogue had m. p. 162—164°. An attempt to prepare this compound by condensation in methyl alcohol solution gave as a by-product, *methyl anisylidenebis*-2-*naphthol*-3-*carboxylate*, $OMe\cdot C_6H_4\cdot CH[C_{10}H_5(OH)\cdot CO_2Me]_2$, in pale yellow, microscopic crystals, m. p. 213—215°.

Cold water precipitated from an acetone solution of the halogen derivatives, *methyl* 1-*α-hydroxy*-p-*methoxybenzyl-2-naphthol-3-carboxylate*, which formed pale yellow leaflets, m. p. 129—130°. The speed of the reaction with water was measured in the case of the α-chlorobenzyl, α-chloro- and α-bromo-anisyl compounds of this series, and the influence of the methoxy-group and the halogen atom were determined. The methoxy-group renders the lability of the halogen atom of the order of an ionic reaction, whilst the bromo-compounds are more reactive than the chloro-. Boiling water gave rise to *methyl* αα′-*oxidobis*-1-p-*methoxybenzyl*-2-*naphthol*-3-*carboxylate*,

$O[CH(C_6H_4\cdot OMe)\cdot C_{10}H_5(OH)\cdot CO_2Me]_2$,

in yellow prisms, m. p. (without crystal solvent) 202—204°.

Methyl alcohol yielded *methyl* 1-α-p-*dimethoxybenzyl*-2-*naphthol*-3-*carboxylate*, $OMe\cdot C_6H_4\cdot CH(OMe)\cdot C_{10}H_5(OH)\cdot CO_2Me$, in pale yellow, glittering tablets, m. p. 176—177°. Ammonia in benzene formed *methyl iminobis*-1-p-*methoxybenzyl*-2-*naphthol*-3-*carboxylate*,

$NH[CH(C_6H_4\cdot OMe)\cdot C_{10}H_5(OH)\cdot CO_2Me]_2$,

as a yellow substance, m. p. 145—148°. With carbamide in boiling acetone, *methyl carbamido*-s-*bis*-1-p-*methoxybenzyl*-2-*naphthol*-3-*carboxylate*, $CO[NH\cdot CH(C_6H_4\cdot OMe)\cdot C_{10}H_5(OH)\cdot CO_2Me]_2$, was obtained as a microcrystalline powder, m. p. 187—189°.

The following α-substituted condensation products were also prepared: α-*anilino*-, faint greenish-yellow, microcrystalline powder, m. p. 191—192°; α-p-*benzeneazoanilino*-, small, orange needles, m. p. 194—195°; α-*benzylamino*-, faintly yellow crystals, m. p. 107—108°; α-*piperidino*-, pale yellow powder, m. p. 166—167°. The basic substituents, in general, give rise to compounds which react in the enolic form, giving intense colours with ferric chloride, but not with strong acids.

The α-hydroxyl and α-anilino-groups were replaced by the methoxy-group, merely on boiling the substances concerned with methyl alcohol. Similarly, hydrogen chloride reconverted the ether or the methoxy-compound into the α-chloro-derivative. J. C. W.

Condensation of Methyl 2:3-Hydroxynaphthoate with *p*- and *m*-Nitrobenzaldehydes. JOSEF SEIB (*Monatsh.*, 1913, 34, 1567—1591).—The influence of the nitro-group on the lability of the halogen atom in compounds analogous to the foregoing has been studied. A rough determination of the speed of the decomposition by cold water showed that the compounds were not half as reactive as

the unsubstituted ones, that the *m*-nitro-derivatives were more active than the para-isomerides and that, as before, bromine in the *a*-position is more labile than chlorine.

Methyl 1-*a-chloro*-p-*nitrobenzyl-2-naphthol-3-carboxylate*,

$$NO_2\cdot C_6H_4\cdot CHCl\cdot C_{10}H_5(OH)\cdot CO_2Me,$$

formed pale yellow, glistening prisms, m. p. 227—228·5°. On boiling with water it yielded the *a-hydroxy*-derivative in lemon-yellow prisms, m. p. 188—190°, which gave the *a-acetoxy*-compound, short prisms, m. p. 185—187·5°, on boiling with acetic anhydride. The *a-methoxy-compound*, formed slender, very pale yellow prisms, m. p. 149—150°; the *ethoxy*-derivative, long, yellow, rectangular tablets, m. p. 116—117°; the *a-phenoxy*-derivative, white needles, m. p. (with 1½ mols. C_6H_6) 181—181·5°; the *a*-p-*tolyloxy*-derivative, pale yellow needles, m. p. 180—180·5°; the *a-thymoxy*-derivative, yellow, microscopic prisms, m. p. [illegible]; the *a-anilino*-derivative, glistening, lemon-yellow tablets, with [illegible]C_6H_6, m. p. 197·5—198°, without crystal solvent, pure yellow, m. p. 199—201°, colourless *hydrochloride*, m. p. 168—171°; the *a*-p-*azobenzeneanilino*-derivative, long, velvety, dark yellow needles, m. p. 154—156°; the *a-benzylamino*-derivative, long, slender, white needles, m. p. 152—153°; the *a-piperidino*-derivative, yellow, rhombic leaflets, m. p. 176·5—177°. In their colour reactions, as before, the compounds with bases exhibit enolic properties, whereas the ketonic form is more pronounced in the remaining compounds.

Pyridine did not cause the total displacement of chlorine, but yielded the *a-pyridinium chloride*,

$$NO_2\cdot C_6H_4\cdot CH(C_5NH_5Cl)\cdot C_{10}H_5(OH)\cdot CO_2Me,$$

in pale yellow, prismatic tablets, m. p. 110°, which were completely hydrolysed in aqueous solution, especially in presence of silver oxide, to pyridine and the *a*-hydroxy-compound.

Methyl 1-*a-bromo*-p-*nitrobenzyl-2-naphthol-3-carboxylate* was obtained in yellow crystals, m. p. 207—208°. Hydriodic acid, however, yielded no crystalline product.

Methyl 1-*a-chloro*-m-*nitrobenzyl-2-naphthol-3-carboxylate* had m. p. 187—189°, and the *bromo*-analogue formed thin, pale yellow leaflets, with $1C_6H_6$, m. p. 177—178°. *o*-Nitrobenzaldehyde, on the contrary, yielded no definite condensation product with methyl 2 : 3-hydroxynaphthoate.

J. C. W.

Hydroxy- and Dihydroxy-diphenylcarboxylic Acids. MATHÄUS MURDROVCIC (*Monatsh.*, 1913, **34**, 1417—1441).—3 : 3′-Dihydroxydiphenyl-4 : 4′-dicarboxylic acid, 3-hydroxydiphenyl-4 : 4′-dicarboxylic acid, and several of their derivatives have been prepared.

Dianisidine was diazotised and converted into the nitrile and this was saponified, with difficulty, by boiling for seventy to eighty hours with alcoholic potassium hydroxide. The crude 3 : 3′-*dimethoxydiphenyl-4 : 4′-dicarboxylic acid*, being only sparingly soluble, was converted into the methyl ester and recovered from this by hydrolysis, as a white, microcrystalline powder, m. p. 270—271·5°. The *potassium* salt, $C_{16}H_{12}O_6K_2,2H_2O$, forms long needles from dilute solutions in spirit, and the *silver* salt is a brown, crystalline powder. The *methyl* ester forms white leaflets, m. p. 170—171°. On heating either the ester or

the acid with hydriodic or hydrobromic acid, 3 : 3′-*dihydroxydiphenyl-4 : 4′-dicarboxylic acid* was obtained as a white, amorphous, sparingly soluble powder, m. p. 318° (decomp.). It gives a colourless solution in sulphuric acid, a deep violet coloration with alcoholic ferric chloride, and apparently forms anhydrides under the influence of thionyl chloride. The *methyl* ester forms slender, colourless needles, m. p. 213—215°, and is readily converted into *methyl* 3 : 3′-*diacetoxydiphenyl-4 : 4′-dicarboxylate*, which crystallises from alcohol in leaflets, m. p. 140—142°.

The methoxy-acid, in contrast to the hydroxy-acid, reacted smoothly with thionyl chloride, forming the *acid chloride*, $C_{16}H_{12}O_4Cl_2$, from a benzene solution of which, ammonia precipitated the *amide*. This forms large needles, $C_{16}H_{16}O_4N_2$,EtOH, from dilute alcohol, m. p. 254—260° (260—261° alcohol-free). On condensing the acid chloride with benzene in presence of aluminium chloride, 3 : 3′-*dihydroxy-4 : 4′-dibenzoyldiphenyl*, $C_{26}H_{18}O_4$, was obtained. The ketone was purified by solution in alkali, reprecipitation by carbon dioxide, heating with hydriodic acid, and crystallisation from alcohol. It forms yellow needles, m. p. 215·5—217·5°, gives a deep yellowish-green, fluorescent solution in sulphuric acid and a reddish-brown coloration with ferric chloride. It was converted by methyl sulphate into 3 : 3′-*dimethoxy-4 : 4′-dibenzoyldiphenyl*, which forms colourless, flat needles, m. p. 156—158°.

As starting material for the preparation of the monohydroxy-compounds, technical ethoxybenzidine was chosen. This was converted into a black, spongy nitrile, which was then hydrolysed as before. Owing to the ready solubility of the acid, however, the crude product could not easily be purified. It was therefore hydrolysed by heating in phenol solution with hydriodic acid, and the crude 3-*hydroxydiphenyl-4 : 4′-dicarboxylic acid* was esterified and recovered by hydrolysis. It forms a white, microcrystalline powder, m. p. 324—325°, crystallises with $1H_2O$ from diluted methyl alcohol, and gives a violet ferric chloride reaction. The *potassium* salt, $C_{14}H_8O_5K_2,H_2O$, and the light brown *silver* salt were prepared. The *methyl* ester forms long, white, glistening needles or leaflets, m. p. 168°, and does not condense with benzaldehyde. *Methyl 3-acetoxydiphenyl-4 : 4′-dicarboxylate* crystallises in very soluble, flat needles, m. p. 119°.

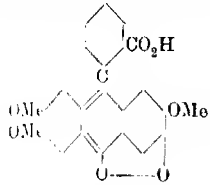
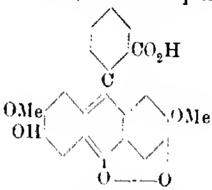
The isomeric mono-esters were prepared according to Wegscheider's directions for hydroxyterephthalic acid (A., 1900, i, 658). Partial hydrolysis of the dimethyl ester with potassium hydroxide yielded 4′-*methyl 4-hydrogen 3-hydroxydiphenyl-4 : 4′-dicarboxylate*, which could be separated from the dicarboxylic acid by benzene, in which the latter is insoluble. It has m. p. 240—241·5° (decomp.), gives a deep violet coloration with ferric chloride, and forms a *potassium* salt. 4-*Methyl 4′-hydrogen 3-hydroxydiphenyl-4 : 4′-dicarboxylate* was obtained in small yield by heating the acid potassium salt with methyl iodide in a sealed tube. It crystallises from benzene in needles, m. p. 215—216°, which give no coloration with ferric chloride.

Schmidt and Schall (A., 1906, i, 23) described 4-hydroxydiphenic acid as a yellow compound. The author also obtained a yellow product,

but on attempting to condense it with benzaldehyde it crystallised as a colourless compound, m. p. 246·5°, the impurity remaining dissolved.

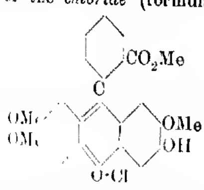
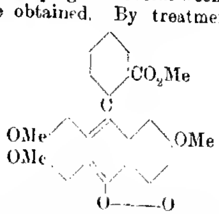
J. C. W.

The Ethers and Esters of Hydroxyquinolphthalein. FRIEDRICH KEHRMANN and RICHARD BERG (*Ber.*, 1913, 46, 3020—3028).—When hydroxyquinolphthalein in solution in sufficient aqueous sodium hydroxide to form the normal salt is warmed with one and two-third times its weight of methyl iodide, the solution on acidification with acetic acid deposits the *trimethyl ether* (formula I), which frequently

(I.)  (II.) 

separates from a mixture of benzene and methyl alcohol in a feebly coloured, presumably lactonoid form; this on recrystallisation from methyl alcohol passes into the quinonoid form, orange-yellow, microscopic leaflets, m. p. 257°; the solution in alkali is yellow with a green fluorescence. The mother liquor from which the trimethyl ether has separated contains the sodium salt of the *dimethyl ether* (formula II), and this substance is deposited as the *hydrochloride* on the addition of concentrated hydrochloric acid; the free ether is liberated from its hydrochloride by the action of sodium acetate solution. This dimethyl ether, m. p. 270—271°, crystallises from methyl alcohol in reddish-brown prisms containing 1MeOH; it dissolves in sodium hydrogen carbonate solution, giving the *sodium* carboxylic salt as a yellowish-red solution with a green fluorescence; addition of sodium hydroxide solution causes the formation of the *disodium* salt, with an increase of the fluorescence; *silver* salt, insoluble reddish-brown precipitate.

On saturating a concentrated methyl-alcoholic solution of the trimethyl ether with hydrogen chloride and keeping for several weeks, needles of the *chloride* (formula III) are obtained. By treatment

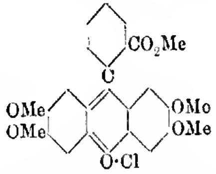
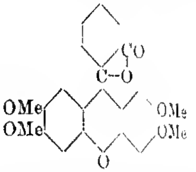
(III.)  (IV.) 

with warm sodium acetate solution, this is converted into the free methyl ester of the trimethyl ether (formula IV), which crystallises from a mixture of benzene and methyl alcohol in orange-yellow, iridescent tablets, m. p. 271—272°.

A similar esterification of the above-mentioned dimethyl ether gives rise to an analogous ester *chloride*, yellow needles, which on decomposition by sodium acetate solution passes into the free *ester* of the dimethyl ether, red crystals, m. p. 248°.

The action of methyl sulphate on a solution of the ester of the trimethyl ether in nitrobenzene solution gave rise to the methyl sulphate salt of the methyl ester of the tetramethyl ether. From this "mixed" sulphate the more ordinary salts were easily obtainable, and their solubility is found to be comparable with those of the corresponding potassium salts; formula V is the *chloride*.

The chloride, *bromide*, and *iodide* are very soluble, the *nitrate*, *chlorate*, *dichromate*, and *persulphate* are moderately soluble, whilst the *perchlorate* and *platinichloride* are sparingly soluble in water. If an aqueous solution of the nitrate is treated in the cold with an excess of

(V.)  (VI.) 

fairly concentrated sodium hydroxide solution, a precipitate is produced, which subsequently redissolves as the *sodium* salt of the tetramethyl ether carboxylic acid; on the addition of acetic acid and warming, the tetramethyl ether lactone (formula VI), colourless prisms, m. p. 292°, is obtained. D. F. T.

Resorcinolbenzein and Fluorescein. FRIEDRICH KEHRMANN (*Ber.*, 1913, **46**, 3028—3036).—A reply to von Liebig (A., 1912, i, 376; this vol., i, 79, 865). In the case of derivatives of fluorescein with which von Liebig obtained results at variance with those of the author and his collaborators, the substances have been reinvestigated with entire confirmation of the earlier results.

It has already been stated by Fischer and Hepp (A., 1895, i, 29) that the quinonoid dimethyl ether of fluorescein crystallises in two forms, namely, orange-yellow needles and deep red prisms. The difference in the m. p.'s recorded by von Liebig and by Kehrmann and Dengler (A., 1909, i, 249) is due to this dimorphism. Indeed, if a quantity of the orange-yellow needles is heated rapidly to 180°, it melts momentarily and resolidifies to melt again at approximately 194°; under similar treatment the red prisms melt at 208°.

The substance, m. p. 255°, obtained by von Liebig by the action of ammonia solution on the ether-insoluble residue (correctly regarded as trimethylfluorescein chloride) from the reaction product of methyl sulphate and disodium fluorescein, is not a dimethyl ether of fluorescein, but contains almost 2% of nitrogen and probably represents a carbinylimide or a carboxylimide. D. F. T.

Synthesis of Depsides, Moss Acids, and Tannins. EMIL FISCHER (*Ber.*, 1913, **46**, 3253—3289).—A lecture before the German

Natural Science Congress (compare A., 1908, i, 892; 1909, i, 161, 555; Fischer and Freudenberg, A., 1910, i, 265; 1911, i, 874; 1912, i, 471, 887; Fischer and Hoesch, A., 1912, i, 859, etc.). The following facts are new. Evernic acid is dissolved by an ethereal solution of diazomethane after a time, and converted into the crystalline neutral ester, which is identified as methyl trimethyl-lecanoric acid. The constitution of evernic acid is thus established. Pentasalicyloglucose and the corresponding derivative of caffeic acid have been prepared, also pentacinnamoyl derivatives of α- and β-glucose, galactose, and mannose. *Penta-acetyl mannose* has m. p. 114—116°, $[\alpha]_D^{20}$ $-24.8°$.

E. F. A.

Humic Acids. IV. Investigations of Tacke and Süchting ELLEN GULLY (*Bied. Zentr.*, 1913, 42, 655—659; from *Mitt. K. Bayr. Moorkulturanst.*, 1912, Heft. 5).—A reply to Tacke and Süchting (A., 1912, i, 473), in which the non-existence of humic acids is maintained. Further experiments showed that peat has no action on calcium oxalate; and that bases absorbed by *Sphagna* can be extracted by water free from carbon dioxide. The various results obtained with peat, such as the liberation of iodine from its salts, the inversion of sucrose, and the production of hydrogen from peat and iron are not considered sufficient evidence that humic acids exist.

N. H. J. M.

The Autoxidation of Organic Compounds. I. Autoxidation of Aromatic Aldehydes. HERMANN STAUDINGER [with E. HENE and J. PRODROM (*Ber.*, 1913, 46, 3530—3535).—It has been previously shown (A., 1911, i, 877) that diphenylketen reacts more readily with methoxy- or dimethylamino-substituted aromatic compounds than with the unsubstituted substances, and similar observations have been made during experiments on the action of oxalyl chloride on carbonyl compounds (A., 1909, i, 905). The authors have therefore been led to the determination of the rate of autoxidation of benzaldehyde and a number of its p-substituted derivatives.

Weighed quantities of benzaldehyde, p-methoxybenzaldehyde, p-hydroxybenzaldehyde, and p-dimethylaminobenzaldehyde were heated with an excess of oxygen in closed flasks at 131° and the amount of oxygen absorbed was estimated. In a second series of experiments, a regular stream of oxygen was bubbled through the aldehyde, the course of the reaction being followed by estimation of the acid formed. At 131°, however, dimethylaminobenzoic acid readily evolved carbon dioxide; a temperature of 80° was found suitable. The results show that p-dimethylaminobenzaldehyde is much less autoxidisable than anisaldehyde, which, however, is less affected than benzaldehyde. This is inexplicable on Engler and Weissberg's hypothesis that the primary product during autoxidation is formed by the addition of a molecule of oxygen to the unsaturated carbonyl group; it is, however, to be expected if Baeyer and Villiger's supposition is adopted that the addition of the oxygen molecule is accompanied by dissociation of the hydrogen atom, $Ph\cdot C\Big\langle{}^{O}_{H} + O\cdot O \longrightarrow Ph\cdot C\Big\langle{}^{O}_{O\cdot O\cdot H}$ (A., 1900, i, 437).

If Staudinger's views as to the asymmetric nature of the intermediate compound are accepted, the hydrogen atom would be more firmly attached to the strongly unsaturated carbonyl group of *p*-dimethylaminobenzaldehyde than to the relatively saturated carbonyl group of benzaldehyde, and therefore less capable of addition to the oxygen molecule. From this point of view, *o*-methoxybenzaldehyde should be the least readily, and *m*-methoxybenzaldehyde the most readily, autoxidisable of the three methoxybenzaldehydes, and this is shown to be actually the case.

Anti-auxochrome groups weaken the unsaturated character of the carbonyl group, and should therefore increase the mobility of the hydrogen atom and the tendency of the substance to autoxidation. *p*-Nitrobenzaldehyde, which should thus be readily autoxidised, absorbs little oxygen, since it is speedily resinified. The problem was, however, investigated by the introduction of acyl groups into amino- and hydroxy-groups. Acetoxybenzaldehyde, in contrast with hydroxy- and methoxy-benzaldehyde, was found to be almost as readily autoxidised as benzaldehyde. H. W.

The Autoxidation of Organic Compounds. II. Relationships between Autoxidation and Benzoin Formation. HERMANN STAUDINGER [with E. HENE] (*Ber.*, 1913, **46**, 3535—3538). —If the possibility of formation of intermediate products be disregarded, the formation of benzoin derivatives from aldehydes is comparable with the autoxidation of the latter substances; in the one case, addition of the aldehyde to the carbonyl group occurs, in the other to the oxygen molecule (compare preceding abstract). A benzoin will only be readily produced, therefore, from an aldehyde which contains a relatively unsaturated carbonyl group and a relatively mobile hydrogen atom; thus, dimethylaminobenzaldehyde does not yield a benzoin, since, although the carbonyl group is strongly unsaturated, the hydrogen atom lacks mobility. Favourable conditions for benzoin formation are found in benzaldehyde, anisaldehyde, and *p*-chlorobenzaldehyde (compare Hantzsch and Glover, A., 1907, i, 538). From this point of view, mixed benzoin derivatives should be obtainable from a pair of aldehydes if the one possesses a sufficiently mobile hydrogen atom, the other a sufficiently unsaturated carbonyl group: the condensation products of *p*-dimethylaminobenzaldehyde and *p*-chlorobenzaldehyde with benzaldehyde are described.

p-*Dimethylaminobenzoin*, $NMe_2 \cdot C_6H_4 \cdot CH(OH) \cdot COPh$, m. p. 163—164°, is obtained in 86% yield when a solution of benzaldehyde and *p*-dimethylaminobenzaldehyde in alcohol is boiled with an aqueous solution of potassium cyanide. The constitution of this substance is deduced from the fact that it condenses with dimethylaniline in the presence of phosphoryl chloride to yield *benzoyltetramethyldiaminodiphenylmethane*, $COPh \cdot CH(C_6H_4 \cdot NMe_2)_2$, pale yellow needles, m. p. 162—164°, which are readily oxidised to a blue dye. Oxidation with Fehling's solution converts *p*-dimethylaminobenzoin into p-*dimethylaminobenzil*, yellowish-green crystals, m. p. 115—116°.

Under similar conditions, *p*-dimethylaminobenzaldehyde condenses

with p-chlorobenzaldehyde to yield p-*chloro*-p′-*dimethylaminobenzoin*, m. p. 127—128°.

Benzaldehyde and anisaldehyde, as also chlorobenzaldehyde and anisaldehyde, appear to yield mixed benzoins. A uniform product could not be isolated. Probably a mixture of benzoins is formed in each case which cannot be separated.

Attempts to prepare benzoins from aromatic and aliphatic aldehydes were unsuccessful. H. W.

The Existence of Mandelaldehyde in Aqueous Solution. W. LLOYD EVANS and CHARLES RAYMOND PARKINSON (*J. Amer. Chem. Soc.*, 1913, 35, 1770—1774. Compare this vol., i, 173).—It is already known that, whereas lactaldehyde is incapable of existence in water at 100° (Nef, A., 1905, i, 3), it is sufficiently stable in water at the ordinary temperature to be studied experimentally (Wohl and Lange, A., 1908, i, 943). Nef has shown that mandelaldehyde also cannot exist in water at 100°, and the present investigation demonstrates that it cannot exist even in the presence of cold aqueous alcohol or of dilute sulphuric acid.

Dibromoacetophenone was converted successively into phenylglyoxal acetal, $CHBz(OEt)_2$, and mandelaldehyde acetal, $CH(OEt)_2 \cdot CHPh \cdot OH$. The last-named substance was found to undergo hydrolysis, yielding benzoylcarbinol, $CH_2Bz \cdot OH$, when suspended in $N/20$-sulphuric acid at 0°, when suspended in water at 0°, or even when exposed to the moisture of the atmosphere. D. F. T.

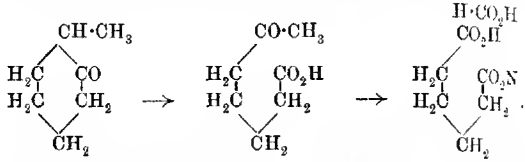
6-Aminopiperonal. AUGUSTE RILLIET and L. KREITMANN (*Compt. rend.*, 1913, 157, 782—784).—Various unsuccessful attempts have been made to prepare the above substance by reduction of 6-nitropiperonal (compare Haber, A., 1891, 704; Friedländer and Schreiber, A., 1895, i, 524). The authors have succeeded by first protecting the aldehyde group.

6-Nitropiperonal condenses readily with various amines to give the corresponding piperonylidene derivatives, of which the following have been prepared: 6-*nitropiperonylidene*-p-*toluidine*, yellow needles, m. p. 121·5°; 6-*nitropiperonylidene*-p-*anisidine*, golden-yellow plates, m. p. 125·5°, and 6-*nitropiperonylidene*-o-*toluidine*, yellow needles, m. p. 128°. All of these are readily reduced in boiling alcoholic solution by sodium sulphide to the corresponding *amino*-compounds, having respectively m. p.'s 134·5°, 162°, and 106°. The hydrolysis of the two latter compounds has not given the desired results, being only brought about with difficulty, but 6-aminopiperonylidene-p-toluidine is readily hydrolysed by prolonged boiling with dilute aqueous alkali, giving 6-*aminopiperonal*, brilliant yellow prisms, m. p. 107°, dissolving in acids to a bright red solution. From it the following derivatives have been prepared: the *mercurichloride*, white needles, decomposing at 135°; a *platinichloride*, a red, amorphous powder, decomposing suddenly on heating; 6-*benzoylaminopiperonal*, pale yellow needles, m. p. 187·5°; 6-*acetylaminopiperonal*, long, white needles, m. p. 161°, yielding a *phenylhydrazone*, white needles, m. p. 205°, and 6-*aminopiperonalphenylhydrazone*, m. p. 222° (decomp.). W. G.

Chemical Action of Light. XXVII. Autoxidation. V. GIACOMO CIAMICIAN and PAUL SILBER (*Ber.*, 1913, **46**, 3077—3084; *Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 339—348).—The action of oxygen and light on acetone, *cyclo*hexanone, the three methyl*cyclo*hexanones, and methylheptenone has been studied. Except in the cases of acetone and methylheptenone (A., 1910, i, 496), the products obtained are due to the combined effect of autoxidation and hydrolysis (compare A., 1908, i, 277).

Acetone yields formaldehyde and acetic acid, whilst *cyclo*hexanone gives hexoic and adipic acids.

1-Methyl*cyclo*hexan-2-one yields *n*-heptoic acid (œnanthoic acid), adipic acid, and acetylvaleric acid, together with traces of aldehyde, the main reaction proceeding in accordance with the scheme:



δ-Acetylvaleric acid has m. p. 31—33°, whilst the semicarbazone melts at 147°. Wallach gives the m. p.'s about 50° and 144—146° respectively (A., 1904, i, 425).

1-Methyl*cyclo*hexan-3-one is less affected than the 1:2-derivative, and gives a heptoic acid, b. p. 215—216°, which must have the constitution $CH_2Me\cdot CH_2\cdot CHMe\cdot CH_2\cdot CO_2H$, a dibasic acid, m. p. 97°, identical with the corresponding compound from 1:4-methyl*cyclo*hexanone, and hence having the formula

$$CO_2H\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot CO_2H,$$

and a lactone which could not be prepared in the pure state.

1-Methyl*cyclo*hexan-4-one gives γ-methylhexoic acid, the above-mentioned dicarboxylic acid and the lactone corresponding with the hydroxy-acid. The latter could not be obtained in a pure condition.

Methylheptenone yields carbon dioxide, acetone, formic acid, acetic acid, and lævulic acid, together with a ketoglycol consisting mainly of the compound $OH\cdot CMe_2\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3$, possibly mixed with the hydroxydiketone, $OH\cdot CMe_2\cdot CO\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3$. Crystalline derivatives could not be obtained, but the identity of the product follows from its conversion by boiling dilute sulphuric acid into β-methylheptane-γζ-dione, $CHMe_2\cdot CO\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3$, and identification of the semicarbazone and dioxime of the latter with the similar compounds obtained by the oxidation of methylheptenone with potassium permanganate (compare Harries, A., 1902, i, 345). The autoxidation of methylheptenone in light proceeds mainly, therefore, according to the scheme: $CMe_2{:}CH\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3 \longrightarrow$

$$OH\cdot CMe_2\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3 \longrightarrow$$
$$OH\cdot CMe_2\cdot CO\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3 \longrightarrow$$
$$CH_3\cdot CO\cdot CH_3 + CO_2H\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3,$$

the acetic and formic acids, as probably also the carbon dioxide, being formed by a partial further oxidation of the acetone. H. W.

Alkylation of 3- and 4-Methyl*cyclo*hexan-3- and 4-ones by means of Sodamide. Albin Haller (*Compt. rend.*, 1913, **157**, 737—743).—Methyl*cyclo*hexan-3- and 4-one not only undergo methylation and allylation under the influence of sodamide, but also ethylation. During the latter reaction condensation of the product on itself is much more pronounced than with the methyl and allyl derivatives. Further, a comparative study of the alkylation of the three methyl*cyclo*hexanones shows that this condensation is much more pronounced the more remote the methyl group is from the ketonic group, and attains its maximum with *cyclo*hexanone itself.

Starting with 1-methyl*cyclo*hexan-3-one, ethyl iodide yields, in ethereal solution in the presence of sodamide, 1-methyl-4-ethyl*cyclo*hexan-3-one (compare A., 1905, i, 214, and Wallach, this vol., i, 482) and 1-*methyl*-2 : 4-*diethyl*cyclo*hexan*-3-*one*, b. p. 216—219°/760 mm., D_4^{20} 0·9061, n_D^{20} 1·4577, together with about 22% of the condensation product. Subsequent successive ethylation of this diethyl derivative furnishes:

1-*Methyl*-2 : 2 : 4-*triethyl*cyclo*hexan*-3-*one*, b. p. 242—244°/770 mm., D_4^{20} 0·9077, n_D^{20} 1·4609.

1-*Methyl*-2 : 2 : 4 : 4-*tetraethyl*cyclo*hexan*-3-*one*, b. p. 266—270°/770 mm., D_4^{20} 0·9358, n_D^{20} 1·4697, having an odour resembling menthone.

1-Methyl*cyclo*hexan-4-ol, b. p. 173—173·5°/760 mm., D_4^{20} 0·9170, n_D 1·4573, obtained by the hydrogenation of *p*-cresol, on oxidation with chromic acid yields 1-methyl*cyclo*hexan-4-one, b. p. 170°/760 mm., D_4^{20} 0·9132, n_D^{20} 1·4458. This ketone on successive methylation under the prescribed conditions with methyl iodide yields:

1 : 3-Dimethyl*cyclo*hexan-4-one (compare Wallach, *loc. cit.*).

1 : 3 : 5-*Trimethyl*cyclo*hexan*-2-*one*, b. p. 184—185°/748 mm., D_4^{20} 0·8992, n_D^{20} 1·4458.

1 : 1 : 3 : 5-*Tetramethyl*cyclo*hexan*-2-*one*, b. p. 190—191°/753 mm., D_4^{20} 0·8903, n_D^{20} 1·4459.

1 : 1 : 3 : 3 : 5-*Pentamethyl*cyclo*hexan*-2-*one*, b. p. 196—198°, D_4^{20} 0·8828, n_D^{20} 1·4461.

Successive introduction of a methyl group produces a regular rise in the boiling point of 6° to 7°, and a steady diminution in the density, whilst the refractive index remains practically constant.

The pentamethyl ketone on hydrogenation with sodium in absolute alcohol yields 1 : 1 : 3 : 3 : 5-*pentamethyl*cyclo*hexan*-2-*ol*, b. p. 203°/760 mm., D_4^{20} 0·8929, n_D^{20} 1·4581, a viscous liquid having an odour resembling that of eugenol.

Progressive ethylation of 1-methyl*cyclo*hexan-4-one similarly yields:

1-*Methyl*-3-*ethyl*cyclo*hexan*-4-*one*, b. p. 196—198°/761 mm., D_4^{20} 0·8996, n_D^{20} 1·4494, having an odour of menthone.

1-*Methyl*-3 : 5-*diethyl*cyclo*hexan*-4-*one*, b. p. 216—218°/765 mm., D_4^{20} 0·9023, n_D^{20} 1·4562, its odour being identical with that of menthone.

1-*Methyl*-3 : 3 : 5-*triethyl*cyclo*hexan*-4-*one*, b. p. 237—240°/758 mm., D_4^{20} 0·9047, n_D^{20} 1·4615.

1-*Methyl*-3 : 3 : 5 : 5-*tetraethyl*cyclo*hexan*-4-*one*, b. p. 258—262°/760 mm., D_4^{20} 0·9301, n_D^{20} 1·4675: a viscous liquid with an odour of turpentine

W. G.

5-Acetylamino-2-hydroxyacetophenone and its Derivatives. FRANZ KUNCKELL (*Ber. Deut. pharm. Ges.*, 1913, **23**, 472—490. Compare A., 1900, i, 663; 1911, i, 990; 1912, i, 268).—2-Hydroxy-5-acetylaminoacetophenone, $NHAc\cdot C_6H_3(OH)\cdot COMe$ (compare Kunckell and Hammerschmidt, this vol., i, 1204), is prepared by the gradual addition of aluminium chloride in bright sunlight to a solution of phenacetin in anhydrous carbon disulphide and acetyl bromide (Schmidt, *Diss.*, 1900) or acetyl chloride (Dirks, *Diss.*, 1906). It forms monoclinic crystals, m. p. 165°. Concentrated hydrochloric acid converts it into 5-*amino-2-hydroxyacetophenone*, yellowish-green needles, m. p. 16[illegible]°, the *hydrochloride*, white leaflets, m. p. 155° (decomp.), and *sulphate*, m. p. 150°, of which are also described. The *phenylhydrazone* of 2-hydroxy-5-acetylaminoacetophenone forms small, yellow needles, m. p. 107°, whilst the *oxime*, white needles, has m. p. 160°; the *nitro*-derivative, $C_{10}H_{10}O_5N_2$, yellow needles, m. p. 170°, is obtained by the gradual addition of concentrated nitric acid to a well-cooled solution of the substance in glacial acetic acid.

When treated with a solution of sodium ethoxide in absolute alcohol, 2-hydroxy-5-acetylaminoacetophenone yields the corresponding *sodium* derivative, lemon-yellow leaflets, m. p. 225° (decomp.), which, when heated with ethyl iodide and ethyl alcohol, is converted into 5-*acetylamino-2-ethoxyacetophenone*, white needles, m. p. 155° (*phenylhydrazone*, brown needles, m. p. 180°; *mononitro*-derivative, yellowish-red needles, m. p. 125°). Attempts to prepare the substance directly by the action of acetyl chloride and aluminium chloride on phenacetin were unsuccessful, the ethyl group being invariably eliminated. Boiling hydrochloric acid converts it into 5-*amino-2-ethoxyacetophenone hydrochloride*, m. p. 215°.

ω-*Chloro-2-hydroxy-5-acetylaminoacetophenone*,

$$CH_2Cl\cdot CO\cdot C_6H_3(OH)\cdot NHAc,$$

yellow needles, m. p. 190°, is prepared by the gradual addition of aluminium chloride in sunlight to a solution of phenacetin and chloroacetyl chloride in carbon disulphide. The free *base*, yellowish-green needles, has m. p. 135°; *hydrochloride*, white leaflets, m. p. 21[illegible]° (decomp.). The *oxime* of 2-hydroxy-5-acetylamino-ω-chloroacetophenone has m. p. 195°.

ω-*Chloromononitro-2-hydroxy-5-acetylaminoacetophenone*, yellow needles, m. p. 160°, is obtained by the gradual addition of concentrated nitric acid to a well cooled solution of ω-chloro-2-hydroxy-5-acetylaminoacetophenone in glacial acetic acid. The *oxime* has m. p. 230° (decomp.). The free *base* forms red needles, m. p. 145° (decomp); the *hydrochloride* of the latter decomposes, without melting, at 210°.

ω-*Chloro-2-hydroxy-5-benzoylaminoacetophenone*,

$$CH_2Cl\cdot CO\cdot C_6H_3(OH)\cdot NHBz,$$

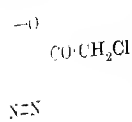
m. p. 203°, is prepared by the action of benzyl chloride on an alcoholic solution of ω-chloro-5-amino-2-hydroxyacetophenone. The corresponding *benzoate* has m. p. 166—167°; the *oxime*, m. p. 197°. The *mononitro*-derivative, yellow needles, m. p. 190° (decomp.), is obtained by nitrating the benzoyl derivative in glacial acetic acid solution.

ω-Chloro-5-amino-2-hydroxyacetophenone couples with a diazotised

...olution of aniline, yielding a *diazoamino*-compound,

$$CH_2Cl\cdot CO\cdot C_6H_3(OH)\cdot NH\cdot N_2Ph,$$

...stable, golden-yellow crystals, m. p. 127°. Attempts to diazotise the base led to the isolation of a *compound* (annexed formula), which explodes without melting at 140°. This substance is decomposed by boiling water, but a pure substance could not be isolated from the product.



The *phenylurethanes* of ω-chloro-2-hydroxy-5-acetylaminoacetophenone and of ω-chloro-5-amino-2-hydroxyacetophenone have m. p.'s 139° and 204° respectively.

The action of phenylhydrazine at a temperature not exceeding 120° on ω-chloro-2-hydroxy-5-acetylaminoacetophenone leads to the formation of the *substance*, $NHAc\cdot C_6H_3(OH)\cdot C(:N\cdot NHPh)\cdot CH:N\cdot NHPh$, needles, m. p. 223°. If the reaction is carried out at a higher temperature and with a relatively smaller quantity of phenylhydrazine, a *substance*, m. p. 247°, is obtained, which has not been completely investigated owing to lack of material. Phenylhydrazine reacts with ω-chloro-5-amino-2-hydroxyacetophenone in a similar manner, yielding the *hydrochloride* of the osazone,

$$HCl,NH_2\cdot C_6H_3(OH)\cdot C(:N\cdot NHPh)\cdot CH:N\cdot NHPh;$$

the pure *osazone*, m. p. 205°, is unstable. H. W.

ε-Aminoketones. KARL A. BÖTTCHER (*Ber.*, 1913, **46**, 3158—3167).—The salts of several benzene-substituted ε-aminoketones have been prepared. Like the simple phenyl ε-aminoamyl ketone in contrast to methyl ε-aminoamyl ketone (Gabriel, A., 1909, i, 492), the new bases do not lose water to form heptacyclic imines, but unlike those simple amines, they yield no definite products under the influence of reducing agents, but are usually unaffected.

Benzoyl-leucine was converted into the chloride, and this condensed with toluene in presence of aluminium chloride. The new benzoyl derivative could not be purified, but was hydrolysed by means of fuming hydrochloric acid in a sealed tube and converted into *tolyl ε-aminoamyl ketone hydrochloride*, $C_{13}H_{20}ONCl$. This salt crystallises in rhombohedra, m. p. 163°, and forms a *platinichloride*, orange-yellow, crystalline powder, m. p. 211°, an *aurichloride*, sulphur-yellow rhombohedra, m. p. 114—116°, and a *picrate*, yellow, jagged crystals, m. p. 148°. The yield of the base was only 18%, but was raised to 41·5% by employing the phthalyl derivative in the condensation. For this purpose, benzoyl-leucine was hydrolysed with fuming hydrochloric acid, the resulting ε-aminohexoic acid was heated with phthalic anhydride, and then converted into ε-phthaliminohexoyl chloride by means of phosphorus pentachloride. On condensation with toluene, the *phthalimino*-derivative, $C_8H_4O_2:N\cdot[CH_2]_5\cdot CO\cdot C_7H_7$, was obtained in well-defined prisms, m. p. 134°. The phthalamino-acid was then prepared by boiling the imide with potassium hydroxide and precipitating with acid, and was finally hydrolysed in a sealed tube. Free *tolyl ε-aminoamyl ketone*, $NH_2\cdot[CH_2]_5\cdot CO\cdot C_7H_7$, was obtained as a colourless oil, b. p. 185—189°/15 mm., m. p. 39—40°, with a basic odour and

strongly alkaline reaction. The *benzenesulphonamide*,

$$C_7H_7\cdot CO\cdot[CH_2]_5\cdot NH\cdot SO_2Ph,$$

formed long, rectangular tablets, m. p. 135—136°. Like the sulphonyl derivative of heptylamine (Marckwald, A., 1900, i, 149) and like *ε-benzoylamylbenzenesulphonamide* [*benzenesulphonyl-ε-aminohexophenone*], $COPh\cdot[CH_2]_5\cdot NH\cdot SO_2Ph$, which was prepared in rhombic tablets, m. p. 84—85°, from ε-benzoylamylamine [ε-aminohexophenone], it did not dissolve in alkalis, but was changed into oily drops on boiling with 33% potassium hydroxide.

ε-Phthaliminohexoyl chloride was also condensed with anisole. The *phthalimino*-derivative, $C_8H_4O_2{:}N\cdot[CH_2]_5\cdot CO\cdot C_7H_7O$, was obtained in leaflets, m. p. 104°, and converted into the *hydrochloride* of ε-p-*methoxybenzoylamylamine* (*ε-anisoylamylamine*) [p-*anisyl ε-aminoamyl ketone*], $OMe\cdot C_6H_4\cdot CO\cdot[CH_2]_5\cdot NH_2,HCl$, which crystallised in thin leaflets, m. p. 166°, and formed a *platinichloride*, sparingly soluble, pale orange, hexagonal leaflets, m. p. 212°; an *aurichloride*, long, orange-yellow rhombohedra, m. p. 118°, and a *picrate*, yellow leaflets, m. p. 135°. The oily base yielded a *phenylthiocarbamide*,

$$C_{13}H_{17}O_2\cdot NH\cdot CS\cdot NHPh,$$

small tablets, m. p. 123°, and a *benzenesulphonamide*, prisms, m. p. 142°.

The following derivatives of ε-*o*-xyloylamylamine [*o*-xylyl ε-aminoamyl ketone] were also prepared: the *phthalimino*-derivative,

$$C_8H_4O_2{:}N\cdot C_{14}H_{19}O,$$

in long needles, m. p. 92°; the *hydrochloride*,

$$C_6H_3Me_2\cdot CO\cdot[CH_2]_5\cdot NH_2,HCl,$$

long leaflets, m. p. 122°; *platinichloride*, pale orange leaflets, m. p. 214°; *aurichloride*, thin, lemon-yellow leaflets, m. p. 129°; *picrate*, jagged leaflets, m. p. 142°. The corresponding derivatives of *m*-xylyl ε-aminoamyl ketone are as follows: *phthalimino*-compound, lanceolate crystals, m. p. 71°; *hydrochloride*, hygroscopic needles, m. p. 88—90°; *platinichloride*, very slender, pale orange needles, m. p. 208°; *aurichloride*, yellow, rectangular, thick tablets, m. p. 99°; *picrate*, small, rectangular, yellow tablets, m. p. 136°. The following derivatives of *p*-xylyl ε-aminoamyl ketone were also prepared: *phthalimide*, needles, m. p. 82°; *hydrochloride*, hexahedra, m. p. 86—87°; *platinichloride*, orange-yellow needles, m. p. 206°; *aurichloride*, thin, yellow leaflets, m. p. 125°; *picrate*, branched needles, m. p. 122°.

Derivatives of ε-3:4-dimethoxybenzoylamylamine [veratryl ε-aminoamyl ketone] are also described: *phthalimide*, tufted needles, m. p. 147°; *hydrochloride*, $(OMe)_2C_6H_3\cdot CO\cdot[CH_2]_5\cdot NH_2,HCl$, small, slender needles, m. p. 106°; *platinichloride*, orange-yellow, slender, branched needles, m. p. 205°; *aurichloride*, ochreous needles, m. p. 165°. The following derivatives of 2:4-dimethoxyphenyl ε-aminoamyl ketone were also prepared: *phthalimide*, long needles, m. p. 117°; *hydrochloride*, tufted leaflets, m. p. 151—152°; *picrate*, tufted prisms, m. p. 167°; *platinichloride*, orange-yellow, flat needles, m. p. 220°; *aurichlorides*, $C_8H_9O_2\cdot CO\cdot[CH_2]_5\cdot NH_2,HCl,2AuCl_3$, from an aqueous solution, yellow leaflets, m. p. 96°, or

$$C_8H_9O_2\cdot CO\cdot[CH_2]_5\cdot NH_2,HCl,AuCl_3,H_2O,$$

from warm 50% acetic acid, orange-yellow prisms, m. p. 96°. Finally,

the following derivatives of 2:5-dimethoxyphenyl ε-aminoamyl ketone are described: *phthalimide*, lanceolate crystals, m. p. 108—109°, which was largely resinified on hydrolysis; *hydrochloride*, yellowish-green, long needles, m. p. 109°; *picrate*, yellow rhombohedra, m. p. 151°; the platini- and auri-chlorides are unstable. J. C. W.

Action of Heat on Ketoximes. ARTHUR KÖTZ and O. WUNSTORF (*J. pr. Chem*, 1913, [ii], 88, 519—530. Compare Angeli and Alessandri, this vol., i, 983).—When heated in the absence of air, ketoximes, which do not distil or sublime without change, undergo decomposition in one of two ways: (1) into ketones, nitrogen, and ammonia: $3CR_2{:}N{\cdot}OH \longrightarrow 3COR_2 + N_2 + NH_3$; (2) into nitriles and aldehydes or alcohols:

$$OH{\cdot}N{:}CPh{\cdot}CH_2Ph \longrightarrow CNPh + CH_2Ph{\cdot}OH$$
$$OH{\cdot}N{:}CPh{\cdot}CHPh{\cdot}OH \longrightarrow CNPh + C_6H_5{\cdot}CHO + H_2O.$$

Acetoxime and *cyclo*hexanoneoxime distil without change under ordinary pressure; at 210—216°, acetoxime decomposes into ammonia, methane, and a mixture of bases, not identified.

When heated in an atmosphere of carbon dioxide, benzophenoneoxime yields benzophenone, nitrogen, and ammonia. Under diminished pressure, acetophenoneoxime may be distilled unchanged, but at ordinary pressures is resolved into acetophenone and ammonia.

Deoxybenzoin decomposes explosively at 270°, yielding benzonitrile, lophine, and benzyl alcohol. At 240°, α-benzoinoxime yields lophine, benzaldehyde, and benzonitrile, whilst oximinocamphor gives rise to camphoric anhydride and αε-dimethyl-Δ^{α}-heptenonitrile (Tiemann, A., 1901, i, 18).

4-Oximino-1-methyl*cyclo*hexan-3-one (Takens, *Diss.*, Göttingen, 1910), m. p. 158—159° or 171°, accordingly as it is slowly or rapidly heated, undergoes complete decomposition when heated in an atmosphere of carbon dioxide above its m. p. F. B.

Polychromic Salts of Oximino-ketones. ISRAEL LIFSCHITZ (*Ber.*, 1913, 46, 3233—3250).—Additional information as to the constitution of chromoisomerides is given by the study of the electrical conductivity of polychromic salt solutions. Oximinodimethyldihydroresorcinol, $CMe_2{<}^{CH_2{\cdot}CO}_{CH_2{\cdot}CO}{>}C{:}N{\cdot}OH$, has been studied as a more simple oximinoketone than violuric acid which contains nitrogen in the ring. The name dimethylviolanic acid is suggested for it. In addition to red and blue, it forms deep green alkali salts indicating that neither the third CO group nor the ring nitrogen in violuric acid are the cause of polychromism. The ring structure is, however, of importance, since oximinoacetylacetone, $(CH_3{\cdot}CO)_2C{:}N{\cdot}OH$, only forms orange to red salts and polychromic forms of the same salt do not exist. Moreover, these coloured salts are unstable. Ring structure alone does not cause polychromism, as neither fluorenoneoxime, benzophenoneoxime, benziloxime, nor oximinodibenzoylmethane exhibit the phenomenon.

When the cornflower-blue plates of sodium dimethylviolanate are

dissolved in methyl alcohol, the solution, likewise cornflower-blue, changes more or less quickly to bluish-green and then to a deep green, when the crystalline green chromoisomeride may be obtained from the solution. At the intermediate stage, it is possible to prepare crystalline, bluish-green or greenish-blue mixed salts. All these solutions contain unimolecular partly dissociated salt, as proved by ebullioscopic measurements.

The green solution is characterised by a new second absorption band in the visible part of the spectrum, and belongs to a new series of chromoisomeric oximino-salts.

The change is rapid only in dilute solutions which are sufficiently dissociated, as it is retarded by additions which check the dissociation. The conductivity of the green isomeride is 2—3% less than that of the blue form.

The two forms differ chemically, the green form being very readily decomposed. In the case of oximinoacetylacetone the cæsium salt decomposes immediately, the rubidium salt can be kept for a time, and the potassium salt is relatively stable. The rate of decomposition, like the depth of colour, increases with the atomic weight of the metal.

Conductivity measurements indicate that dimethylviolanic acid contains yellow oxime ions, and has the structure

$$CMe_2<\begin{matrix}CH_2\cdot CO\\CH_2\cdot CO\end{matrix}>C:N\cdot OH,$$

whereas the blue sodium salt is derived from a blue acid having a higher dissociation constant, and probably the nitrosoenol structure, $CMe_2<\begin{matrix}CH_2\cdot C(OH)\\CH_2\text{——}CO\end{matrix}>C\cdot NO$. This result is in agreement with the optical behaviour.

The behaviour of the blue potassium salt and the red lithium salt of diphenylvioluric acid in methyl alcohol and in acetone indicates that the red lithium salt in acetone contains an internal alkali complex salt, whereas in the violet-red solution in methyl alcohol this complex has decomposed. Probably the yellowish-red and violet salts are not mixed salts, but their isomerism is not due to differences in partial valency. The copper-red magnesium dimethylviolanate forms a violet-red solution in water, and a red solution of very low conductivity in organic solvents.

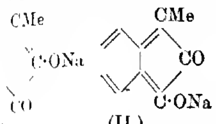
The green sodium dimethylviolanate is considered to have the structure $CMe_2<\begin{matrix}CH_2\text{——}CO\\CH_2\cdot C(ONa)\end{matrix}>C\cdot NO$.

Dimethylviolanic acid is prepared as described by Haas (T., 1906, **89**, 189). The *methyl* ester forms a yellow, crystalline crust, m. p. 92°. The *magnesium* salt forms lustrous, bright copper-red platelets; the *copper* salt separates in brown platelets with a bronze lustre; the *silver* salt, $2H_2O$, forms a dark green, microcrystalline powder.

Phenylviolanic acid, $CHPh<\begin{matrix}CH_2\cdot CO\\CH_2\cdot CO\end{matrix}>C:N\cdot OH$, is a pale yellowish-green, crystalline powder, m. p. 175°. When warmed with water a chocolate-brown, lustrous powder is obtained.

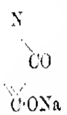
The alkali salts of oximinoacetylacetone are described. E. F. A.

3-Methyl-1 : 2-diketohydrindene, an Analogue of Isatin. JULIUS VON BRAUN and G. KIRSCHBAUM (*Ber.*, 1913, **46**, 3041—3050).—*3-Methyl-1 : 2-diketohydrindene* is readily obtained by the action of cold formaldehyde and hydrochloric acid on oximino-3-methylhydrindone (compare Perkin, Roberts, and Robinson, T., 1912, **101**, 232). It strongly resembles isatin, having a deep reddish-yellow colour, giving the same indophenine reaction, and dissolving in alkali with a very intense bluish-violet colour, which is much more stable than the corresponding coloration from isatin. Of the two possible formulæ (I. and II.) for the sodium salt, the authors are led to prefer (II.), since the great change in colour from red to bluish-violet is better explained (especially in view of the fact that the salts of 2-methyldiketohydrindene which must have a structure similar to that of formula I, are red), whilst, also, the free diketone gives no coloration with ferric chloride, and does not combine with bromine, that is, it has no tendency towards enolisation of the usual type.



(I.) (II.)

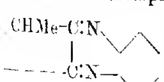
With benzoyl chloride, the sodium salt of 1 : 2-diketo-3-methylhydrindene yields 1 : 2-*diketo-3-benzoyl-3-methylhydrindene*, which is readily explained by 1 : 4-addition. In this light, the authors are led to propose the annexed formula for the bluish-violet salts of isatin prepared by Heller (A., 1907, i, 442), and find confirmation, therefore, in the fact, that all derivatives of isatin, in which, the carbonyl group adjacent to the NH group is substituted and which themselves are red or brown, yield blue solutions with alkali, whilst derivatives in which the β-carbonyl group is substituted yield yellow or brown solutions with alkali.



3-Methyl-α-hydrindone, b. p. 118—119°/11 mm., is obtained as a pale yellow oil which could not be caused to solidify by the action of aluminium chloride on a solution of β-phenylbutyryl chloride in light petroleum. The oily *phenylhydrazone*, *semicarbazone*, m. p. 230—231°, *oxime*, m. p. 141·5°, *benzylidene* derivative, m. p. 88—89°, and *salicylidene* derivative, yellow needles, m. p. 172°, were analysed. The regulated action of amyl nitrite and hydrochloric acid on an alcoholic solution of 3-methyl-α-hydrindone leads to the formation of the somewhat unstable oximinomethylhydrindone,

$$C_6H_4<{CHMe \atop CO}>C:N\cdot OH,$$

almost colourless crystals, m. p. 130°, which readily yields a *benzoyl* derivative, m. p. 125°. Cold concentrated hydrochloric acid and formaldehyde convert the oximino-derivative into 1 : 2-diketo-3-methylhydrindene, which is obtained as a viscous red oil which could not be distilled without decomposition and did not solidify. It yields a *disemicarbazone*, m. p. 267° (decomp.), and condenses with *o*-phenylenediamine in warm methyl-alcoholic solution to a *quinoxaline* derivative (annexed formula), m. p. 202°. It dissolves instantly in



aqueous alkali with the formation of an intensely bluish-violet solution, which, in comparison with the similar solutions obtained from isatin or 1 : 2-diketohydrindene, is remarkably stable; after four hours the colour commences to disappear, whilst after five hours the solution is dirty brown. Addition of acid then precipitates an *acid* which softens at 133°, and has m. p. 143° (decomp.). This substance could not be obtained pure, but probably has the composition

$$C_6H_4Et\cdot CO\cdot CO_2H.$$

The rupture of the ring occurs more easily after benzoylation. When benzoyl chloride is added to an alkaline solution of the ketone, the *benzoyl* derivative, $C_{17}H_{12}O_3,H_2O$, m. p. 195° (decomp.), is precipitated, and the alkaline filtrate yields on acidification benzoic acid and a *diketo-acid*, $C_{17}H_{14}O_4$, m. p. 203°, which gives a *diphenylhydrazone*, $C_{29}H_{26}O_2N_4$, m. p. 238°, reaction occurring according to the scheme:

$$C_6H_4{<}{\genfrac{}{}{0pt}{}{CMe{-}{-}}{C(ONa)}}{>}CO \longrightarrow C_6H_4{<}{\genfrac{}{}{0pt}{}{CMeBz}{CO{-}{-}}}{>}CO \longrightarrow C_6H_4{<}{\genfrac{}{}{0pt}{}{CHMeBz}{CO\cdot CO_2H}}$$

Methylhydrindone differs remarkably from hydrindone in its behaviour towards Grignard's reagents. Whereas the latter reacts vigorously with methyl magnesium iodide, yielding 1-*hydroxy-1-methylhydrindene*, $C_6H_4{<}{\genfrac{}{}{0pt}{}{CH_2{-}{-}}{CMe(OH)}}{>}CH_2$, b. p. 118°/14 mm., D_4^{20} 1·068, which can be distilled under ordinary pressure without notable elimination of water, the tertiary alcohol primarily formed from 3-methylhydrindone by a similar process loses the elements of water almost completely at 90°, and forms 1 : 3-*dimethylindene*,

$$C_6H_4{<}{\genfrac{}{}{0pt}{}{CHMe}{-CMe}}{>}CH,$$

b. p. 212—214°/ordinary pressure, 86—88°/11 mm., D_4^{20} 0·9553, n_D^{20} 1·53444, which, unlike methylindene, is practically stable to air. It forms a *picrate*, yellow needles, m. p. 94—95°. H. W.

1 : 2-Diketo-3-methylhydrindene. A Correction. JULIUS VON BRAUN (*Ber.*, 1913, **46**, 3250. Compare preceding abstract).—The author has inadvertently overlooked the fact that the views advanced by him on the constitution of salts of isatin have been previously advocated by Ruhemann, T., 1909, **95**, 984). H. W.

Diacetyldi-imino-α-naphthol and its Transformations. IV. OSWALD MILLER (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1480—1488. Compare this vol., i, 877).—Neither Meerson (A., 1888, 713) nor Kehrmann (A., 1895, i, 151) succeeded in obtaining diacetyldi-imino-α-naphthol by the action of acetic anhydride and sodium acetate on di-imino-α-naphthol hydrochloride. The latter, as the author has already pointed out (A., 1911, i, 308), crystallises with $2H_2O$, which partly decomposes the diacetyl compound at the moment of its formation; the inaccuracy of Meerson's view that acetic anhydride plays a part in this decomposition, is evident from the fact that diacetyldi-imino-α-naphthol may be crystallised from this solvent, as from any other free from hydroxyl ions, without undergoing any decomposition.

Diacetyldi-imino-α-naphthol, $C_{14}H_{12}O_3N_2$, obtained by the action of

acetic anhydride and sodium acetate on anhydrous di-imino-α-naphthol hydrochloride, forms yellow prisms, m. p. 187°, and dissolves in fuming nitric acid or acetic acid with production in almost theoretical yields of acetylamino-1 : 4-naphthaquinone. The latter (1 mol.) combines with diacetyldi-iminonaphthol (1 mol.) to give the compound, $C_{14}H_{14}O_3N_2,C_{12}H_9O_3N$, m. p. 178° (decomp.), described by Meerson (loc. cit.). Decomposition of diacetyldi-iminonaphthol by heating in aqueous alcoholic solution results in the formation of four parts of 2-acetylamino-1 : 4-naphthaquinone and 1 part of 4-acetylamino-1 : 2-naphthaquinone.

The action of a glacial acetic acid solution of aniline on a solution of diacetyldi-iminonaphthol in 95% alcohol yields a mixture of the ordinary dianilide with a new anilide, *2-acetylamino-4-phenylimino-1 : 4-naphthaquinone*, $C_{18}H_{14}O_2N_2$, which crystallises in yellowish-red needles, or in red plates with marked metallic lustre, m. p. 185°; by boiling acetic acid it is decomposed quantitatively into aniline and acetylamino-1 : 4-naphthaquinone. Its *platinichloride*,

$$(C_{18}H_{14}O_2N_2,HCl)_2,PtCl_4,$$

which forms yellowish-brown plates, is accompanied by that of 2-amino-4-phenylimino-1 : 4-naphthaquinone, m. p. 121° (compare Miller and Smirnov, A., 1911, i, 121). Thus, this new anilide, like the derivatives of naphthaquinones already investigated, shows a marked tendency to react in two directions.

The above method of obtaining the new anilide leads also to the formation of three compounds of this anilide with the dianilide: (1) $2C_{18}H_{14}O_2N_2,C_{22}H_{16}ON_2$, which forms reddish-yellow plates, m. p. 170—171°; (2) $1{\cdot}66C_{18}H_{14}O_2N_2,C_{22}H_{16}ON_2$, which forms red plates, m. p. 147—148°; (3) red needles and plates, m. p. 160°. The melting points of these compounds rise on melting and re-solidification.

T. H. P.

The Three Isomeric Di-α-naphthoylbenzenes. Christian Seer and Otto Dischendorfer (*Monatsh.*, 1913, **34**, 1493—1502).—The *p*- and *m*-di-α-naphthoylbenzenes have been prepared by condensing terephthalyl chloride and *iso*phthalyl chloride respectively, with naphthalene in cold carbon disulphide solution, by means of aluminium chloride. Since phthalyl chloride reacts in the unsymmetrical form, and α-naphthoyl-*o*-benzoyl chloride will not react in the cold, such a condensation could not be carried out for the ortho-isomeride. The latter was obtained, however, from α-naphthoyl-*o*-benzoic acid by Guyot and Vallette's method (A., 1911, i, 652).

The yield of crude, light brown p-*di-α-naphthoylbenzene*,

$$C_6H_4(CO{\cdot}C_{10}H_7)_2,$$

was very high, but the compound was obtained crystalline with great difficulty, by distilling the crude product, dissolving the oily distillate, b. p. 315—330°/11—20 mm., in boiling glacial acetic acid, and filtering from resinous matter as soon as crystals appeared. It forms, colourless, glistening leaflets, m. p. 233—234°, and gives a blood-red solution in sulphuric acid. m-*Di-α-naphthoylbenzene* was also obtained in good yield in colourless, glistening leaflets from dilute pyridine, m. p. 191°.

α-Naphthoyl-*o*-benzoic acid was reduced by zinc and 80% acetic acid,

when the *lactone* of *phenyl-α-naphthylcarbinol*-o-*carboxylic acid*,

$$C_{10}H_7\cdot CH<\overset{O}{\underset{C_6H_4}{}}>CO,$$

crystallised on cooling. It was purified by extraction with boiling dilute hydrochloric acid, and formed faintly yellow spikelets from alcohol, m. p. 135—136°. The lactone was treated with magnesium α-naphthyl bromide, and the white, flocculent magnesium compound was decomposed with dilute hydrochloric acid, when 2 : 5-*di-α-naphthyl-3 : 4-benzofuran*, $C_6H_4<\begin{matrix}C(C_{10}H_7)\\C(C_{10}H_7)\end{matrix}>O$, was obtained in bright yellow, glistening needles, m. p. 166°, which give deep yellow solutions with brilliant green fluorescence. On oxidation with sodium dichromate and acetic acid, a quantitative yield of o-*di-α-naphthoylbenzene* was obtained. This isomeride is freely soluble, forms colourless needles, m. p. 130—131°, and condenses with hydrazine hydrate to 1 : 4-*di-α-naphthylphthalazine*, $C_6H_4<\begin{matrix}C(C_{10}H_7):N\\C(C_{10}H_7):N\end{matrix}$, which crystallises in rhombic plates, m. p. 176°.

Attempts to prepare condensation products by heating these isomeric diketones with aluminium chloride were without success.

J. C. W.

Preparation of Bromoaminoanthraquinones. Badische Anilin- & Soda Fabrik (D.R.-P. 263395, 265727. Compare this vol., i, 1071).—The preparation of 3-bromo-2-aminoanthraquinone from 1-bromo-2-aminoanthraquinone-3-sulphonic acid by elimination of the sulphonic group (with sulphuric acid) and migration of the bromine atom has been previously described; and it is now found that this reaction is a general one when a bromine atom, amino- and sulphonyl group are all present in the same benzene nucleus.

3 : 7-Dibromo-2 : 6-diaminoanthraquinone is prepared by heating sodium 1 : 5-dibromo-2 : 6-diamino-3 : 7-disulphonate with 20 parts of sulphuric acid (60° Bé.) at 180—190°; it does not react with aniline.

3 : 6-*Dibromo*-2 : 7-*diaminoanthraquinone* is obtained in a similar manner from 1 : 8-dibromo-2 : 7-diaminoanthraquinone-3 : 6-disulphonic acid, and does not react with aniline or *p*-toluidine.

4-*Bromo*-1-*aminoanthraquinone*-2-*sulphonic acid* is obtained by sulphonating, and subsequently brominating (in aqueous solution), 1-aminoanthraquinone; when it is boiled with concentrated sulphuric acid it gives rise to 2-bromo-1-aminoanthraquinone (*loc. cit.*).

The second patent states that if the heating in the reactions described previously is carried out for a few moments only in the presence of mercury (or its salts) that the sulphonic group is eliminated, but the migration of the bromine atom does not occur; thus, when sodium 1-bromo-2-aminoanthraquinone-3-sulphonate (10 parts) is heated with 100 parts of sulphuric acid (66° Bé.) and mercury sulphate (0.5 part) at 180° during three minutes, it gives rise to 1-bromo-2-aminoanthraquinone, which readily furnishes 2-*amino*-1-p-*toluidinoanthraquinone* with *p*-toluidine, whilst 4-bromo-1-aminoanthraquinone-2-sulphonic acid gives rise to 4-bromo-1-aminoanthraquinone.

F. M. G. M.

Bromohydroxynaphthaquinones. V. OSWALD MILLER (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1467—1479).—The author finds that the dibromide, m. p. 149·5—151·5°, described by Diehl and Merz (*Ber.*, 1881, **14**, 1912) does not exist, and establishes the identity of the bromohydroxynaphthaquinones prepared from: (1) the dibromide, m. p. 218° (compare Miller, A., 1885, 667); (2) 2-hydroxy-α-naphthaquinone (compare Diehl and Merz, A., 1878, 888); (3) α-naphthaquinoneanilide (compare Balzer, A., 1882, 204), and (4) bromo-β-naphthaquinone (compare Zincke, A., 1887, 53). In the last of these methods, which is aerobic, only one-third of the oxygen absorbed reacts according to the equation $C_{10}H_{15}O_2Br + O = C_{10}H_5O_3Br$, the remaining two-thirds acting on a second molecule of the bromonaphthaquinone to form secondary products.

3-*Bromo-2-hydroxy-1:4-naphthaquinone*, $C_6H_4<\begin{matrix}CO\cdot C(OH)\\ \| \\ CO\cdot CBr\end{matrix}>$, crystallises in monoclinic prisms or hemihedral forms, m. p. 198·5° (corr. 202°). The canary-yellow colour of the powdered compounds persists on heating to 170°, at which temperature a number of orange-yellow spots make their appearance. These spots gradually increase in magnitude as the temperature is raised, until at 190° the whole mass exhibits the orange-yellow colour, the powder becoming converted at the same time into small prisms. On cooling, these prisms become somewhat paler and undergo disintegration. The golden-yellow liquid obtained on fusion solidifies only at about 170°, but subsequently melts as before at 198·5°. The identity of the products yielded by the different methods of preparation was ascertained by investigation of (1) the solubility in 95% alcohol; (2) the potassium salt, which is anhydrous; (3) the barium salt $(+4H_2O)$, and (4) the aniline salt, m. p. 166·5° (decomp.). The homogeneity of the compound was established by heating it at various temperatures for ten hours, the non-volatilised residues in all cases melting at 198·5°.

The yields of phthalic acid obtained by oxidising various naphthaquinone derivatives by means of potassium permanganate in sulphuric acid solution are: α-naphthaquinone, 95·2%; 2-hydroxy-α-naphthaquinone, 93·4%; bromohydroxynaphthaquinone from Miller's dibromide, m. p. 218°, 96·4%; bromohydroxynaphthaquinone from 2-hydroxy-α-naphthaquinone, 97·3%. These results are regarded as a confirmation of the ordinary structural formula for naphthalene.

T. H. P.

Purpurogallin. I. MAXIMILIAN NIERENSTEIN and C. W. SPIERS (*Ber.*, 1913, **46**, 3151—3157).—The authors have oxidised pyrogallol by several processes, and have shown that the purpurogallin obtained is identical in all cases. This substance has the formula $C_{11}H_8O_5$, contains four free hydroxyl groups (estimated by Zerevitinov's method, A., 1908, i, 593, in a modified apparatus) and a carbonyl group, and yields naphthalene on distillation with zinc dust. The oxidation was effected by the following means: with sodium nitrite and acetic acid (Perkin and Steven, T., 1903, **83**, 197), which is the best method, and yields 10—16% of the substance; with silver nitrate or acid permanganate (Girard, 1869); with chromic acid or *p*-benzoquinone

(Wichelhaus, A., 1872, 172, who called the compound, in the latter case, pyrogalloquinone, and obtained quinol as a by-product); by passing a current of air through a solution of pyrogallol and gum arabic (Struve, A., 1872, 703); with horse-radish peroxydase; with potassium ferricyanide (Hooker, A., 1888, 292), and by electrolysis (Perkin and Perkin, T., 1904, 85, 243).

Purpurogallin was obtained in deep-red needles from glacial acetic acid. It always melted at 274—275° in a sulphuric acid bath, but in a paraffin bath, or in very long capillary tubes, it sublimed without melting.

Tetra-acetylpurpurogallin was easily prepared in orange-yellow needles, m. p. 179—180° (Herzig, A., 1910, i, 677, described a colourless product). The molecular-weight determinations with certain solvents gave abnormal results, which could be explained in the case of acetic acid by partial hydrolysis to *monoacetylpurpurogallin*, which formed brownish-red needles, m. p. 169—170°; these could be separated mechanically. The tetra-acetyl derivative was completely hydrolysed by 50% acetic acid, and readily formed a *phenylhydrazone*, $C_{11}H_4O_4(COMe)_4$:N·NHPh, in brick-red needles, m. p. 254—258°.

The authors are studying the formation of hydroxy-*o*-benzoquinone, which Wichelhaus, Perkin and Steven, and Perkin (T., 1913, 104, 661) have assumed to represent an intermediate stage in the oxidation of pyrogallol. J. C. W.

Preparation of Nitrogenous Condensation Products of the Anthraquinone Series. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 265725).—When aminoanthraquinones are heated at 200—220° with naphthols in the presence of zinc chloride they furnish condensation products which are formed from 1 molecule of the aminoanthraquinone and 2 molecules of the naphthol, with elimination of 3 molecules of water. The following *compounds* are described: (1) from 1-aminoanthraquinone with β-naphthol, a red, crystalline powder; (2) from 2-aminoanthraquinone with β-naphthol, a yellowish-red, crystalline powder; (3) from 1-aminoanthraquinone with α-naphthol, a dark violet powder, and (4) from 4-chloro-1-aminoanthraquinone with β-naphthol, a red, crystalline powder. F. M. G. M.

Retene. III. Condensation of Retenequinone with Ketonic Compounds. ALFRED HEIDUSCHKA and CH. KHUDADAD (*Arch. Pharm.*, 1913, 251, 401—437. Compare A., 1912, i, 107).—Retenequinone, which resembles benzil and phenanthraquinone in its behaviour towards organomagnesium haloids (Heiduschka and Grimm, *loc. cit.*), has been examined as to its behaviour during condensation with various types of ketones, to ascertain whether its analogy to benzil and phenanthraquinone is also evident in such reactions. In the presence of aqueous or, better, alcoholic potassium hydroxide, retenequinone (1 mol.) condenses with only 1 mol. of an aliphatic ketone, CH_2R·COMe (where R may be hydrogen and no negative group, other than the carbonyl, is present) to form, unlike benzil and phenanthraquinone, only one product. Four formulæ are possible for the substance, but the two containing >C:CR· are excluded because the condensation product is rapidly attacked by Baeyer's reagent, whereby the presence

of the group $>C:CH\cdot$ is indicated. The condensation product, therefore, may have the constitution : $C_{16}H_{16}<\begin{matrix}C:CH\cdot CO\cdot CH_2R\\ |\\ CO\end{matrix}$ or

$$C_{16}C_{16}<\begin{matrix}C{=\!=\!=}CH\\ |\\ C(OH)\cdot CHR\end{matrix}>CO;$$

the first, however, is excluded because the substance, except where R is hydrogen, does not condense with benzaldehyde in alkaline solution, thereby showing that a methyl or methylene group adjacent to a carbonyl group is not present.

Anhydroacetoneretenequinone, $C_{16}H_{16}<\begin{matrix}C{=\!=\!=}CH\\ |\\ C(OH)\cdot CH_2\end{matrix}>CO$, m. p. 206·5°, colourless needles, does not react with phenylhydrazine or with phenylcarbimide in the cold, condenses with benzaldehyde in the presence of alcoholic potassium hydroxide to form a *substance*, $C_{..}H_{24}O_2$, m. p. 203—204° (decomp.), pale yellow needles, and is reduced by zinc dust and acetic acid to a *substance*, $C_{21}H_{20}O$, m. p. 201°, colourless needles. *Methylanhydroacetoneretenequinone*,

$$C_{16}H_{16}<\begin{matrix}C{=\!=\!=}CH\\ |\\ C(OH)\cdot CHMe\end{matrix}>CO,$$

m. p. 205°, colourless needles, obtained together with a small quantity of an isomeride from methyl ethyl ketone, forms a *dibromide*, $C_{..}H_{22}O_2Br_2$, m. p. about 195° (decomp.), and is reduced to a *substance*, probably $C_{16}H_{16}<\begin{matrix}C{-\!-}CH_2\\ \|\\ C\cdot CHMe\end{matrix}>CO$, m. p. 153—155°, by zinc dust and acetic acid, or by boiling hydriodic acid, D 1·96, and to a *substance*, $C_{..}H_{24}O$, m. p. 192—193° (decomp.), by zinc and alcoholic hydrochloric acid. Retenequinone and methyl propyl ketone yield *ethylanhydroacetoneretenequinone*, $C_{23}H_{24}O_2$, m. p. 186—187°, colourless needles. Retenequinone condenses with methyl hexyl ketone and with methyl hexenyl ketone to form corresponding *substances*, $C_{..}H_{30}O_2$, m. p. 181—182°, and $C_{26}H_{28}O_2$, m. p. 213—214°, both colourless needles, and with mesityl oxide (only in the presence of alcoholic potassium hydroxide) to form iso*propylideneanhydroacetoneretenequinone*, $C_{24}H_{24}O_2$, m. p. 219°.

Retenequinone and benzyl methyl ketone in the presence of aqueous potassium hydroxide yield two *substances*, one, probably

$$C_{16}H_{16}<\begin{matrix}C:CPh\cdot COMe\\ |\\ C:CPh\cdot COMe\end{matrix},$$

m. p. 200—202° (decomp.), faintly red crystals, the other, $C_{45}H_{40}O_2$, m. p. 214—215°, deep red crystals; the residue from the mother liquor, by boiling with glacial acetic acid, yields a *substance*, $C_{29}H_{26}O_3$, m. p. 210—212°, colourless needles, which is *phenylanhydroacetoneretenequinone acetate*, since it is also obtained by heating phenylacetoneretenequinone with glacial acetic acid. *Phenylacetoneretenequinone*, probably $C_{16}H_{16}<\begin{matrix}C(OH)\cdot CHPh\cdot COMe\\ |\\ CO\end{matrix}$, m. p. 190—192° (decomp.), yellow crystals, is obtained from retenequinone and benzyl methyl ketone in the presence of alcoholic potassium hydroxide.

Retenequinone and ethyl acetonedicarboxylate in the presence of

alcoholic potassium hydroxide condense to form a *substance*, $C_{27}H_{28}O_5$, m. p. 185—187° (decomp.), yellow needles or leaflets, which receives the constitution $C_{16}H_{16}<\begin{matrix}C\text{=====}C(CO_2Et)\\ C(OH)\cdot CH(CO_2Et)\end{matrix}>CO$.

Retenequinone and ethyl benzoylacetate, by treatment with acetic anhydride and a little concentrated sulphuric acid at 45—50° yield a *substance*, $C_{40}H_{36}O_6$, m. p. 235°, faintly yellow needles, which is probably $C_{16}H_{16}<\begin{matrix}C{:}CBz\cdot CO_2Et\\ C{:}CBz\cdot CO_2Et\end{matrix}$. C. S.

Action of Zinc on a Mixture of Fenchone and Allyl Iodide. MICHAEL ZAJCEV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 1578—1580).—The action of zinc on a mixture of fenchone and allyl iodide in presence of ether yields *allylfenchyl*, $C_{13}H_{22}O$, b. p. 107—109°, D_0^0 0·9747, D_{20}^{20} 0·96144, D_4^{20} 0·9597, $[\alpha]_D$ +12·44°, n_D 1·49143. Attempts to prepare the corresponding *chloride*, $C_{13}H_{21}Cl$, by saturating allylfenchyl with dry hydrogen chloride in the cold, yielded an impure product, b. p. 122—124°. The investigation is being continued. T. H. P.

Synthesis of 3-Ethylpulegol. MICHAEL ZAJCEV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 1571—1577).—The preparation of 3-methylpulegol by the action of magnesium and methyl bromide on pulegone was unsuccessfully attempted by Grignard (A., 1901, i, 679), and by Rupe and Emmerich (A., 1908, i, 556), and this compound has only recently been prepared (compare Rupe, Schobel and Abegg, A., 1912, i, 573). The corresponding ethyl compound is, however, readily obtainable.

3-*Ethylpulegol*, $CHMe<\begin{matrix}CH_2\cdot CEt(OH)\\ CH_2\text{——}CH_2\end{matrix}>C{:}CMe_2$, has b. p. 105—110°/9 mm., D_0^0 0·9379, D_{20}^{20} 0·9239, D_4^{20} 0·9223, $[\alpha]_D^{20}$ +43·22°, and exhibits normal cryoscopic behaviour in benzene. When oxidised by means of permanganate, it yields (1) the *trihydric alcohol*,

$$CHMe<\begin{matrix}CH_2\cdot CEt(OH)\\ CH_2\text{——}CH_2\end{matrix}>C(OH)\cdot CMe_2\cdot OH,$$

which is a viscous, cinnamon-coloured liquid; (2) β-methyladipic acid, (3) formic acid, and other products. T. H. P.

Chemistry of Caoutchouc. VII. Theory of Vulcanisation. V. DAVID SPENCE and J. YOUNG (*Kolloid. Zeitsch.*, 1913, 13, 265—271. Compare A., 1912, i, 706).—Further experiments have shown that there is no lower limiting temperature, as previously suggested, below which vulcanisation does not take place. By extending the period of observation it has been found that vulcanisation occurs at 50°, and from experiments made at intervals of 5° between 50° and 75°, the velocity of the vulcanisation process increases on the average in the ratio of 2·84 : 1 for a rise of temperature of 10°. The value of the temperature-coefficient lends support to the view that the vulcanisation process is a chemical change.

From comparative experiments on the speed of the vulcanisation

of caoutchouc, gutta-percha, and balata at 135°, it appears that the rate of the change is practically the same in all three cases. In each case, also, the vulcanisation reaches a limit when the quantity of sulphur, non-extractable with acetone, amounts to 32%. This proportion of sulphur corresponds with the formula $(C_{10}H_{16}S_2)_n$, and it is supposed that this compound is formed from each of the three substances.

The difference between caoutchouc, gutta-percha, and balata is considered to have its origin in differences in the colloidal condition of the hydrocarbon, the close similarity in the behaviour on vulcanisation being entirely opposed to the view that the differences are chemical in nature. H. M. D.

Formation of the Anthocyan Pigments of Plants. VI. FREDERICK KEEBLE, E. FRANKLAND ARMSTRONG, and W. NEILSON JONES (*Proc. Roy. Soc.*, 1913, *B*, **87**, 113—131. Compare A., 1912, ii, 673; this vol., i, 325, 803).—The pale yellow sap colour of the petals of the wallflower is a mixture of hydroxyflavone glucosides (compare A. G. Perkin, T., 1896, 1566; Perkin and Pilgrim, T., 1898, 267). The mixture is hydrolysed by heating with acids and more slowly by emulsin. The hydrolysed pigment if reduced and subsequently oxidised yields a red pigment. A red pigment is obtained from most flowers containing similar soluble yellow pigments, suggesting that red mutations should be of possible occurrence in such species.

Oxidation by oxydase of the hydrolysed products of glucosides in presence of amino-acids yields pigments. Arbutin, for example, yields a red pigment probably produced by the interaction of quinhydrone with ammonia. It is suggested that many of the pigments and odorous substances formed during the ripening of fruits arise as results of reactions of this type.

A competition for oxydase ensues when a mixture of phenols is treated with a plant oxydase.

Quinol monomethyl ether gives no colour reaction with oxydase, but when a little benzidine solution is added, a deep and persistent carmine colour is obtained. The benzidine acts catalytically, playing the part of an organic peroxide, and bringing about the oxidation of a substance which resists the action of oxydase and hydrogen peroxide. It is suggested that the higher members of a flower colour series owe their origin to the presence of specific substances which, acting as receivers of oxygen, reduce the pigments characteristic of the lower members of the colour series, accept oxygen therefrom, and become oxidised to pigments of specific colour. E. F. A.

Anthocyanins. I. Pigment of Cornflowers. RICHARD WILLSTÄTTER and ARTHUR E. EVEREST (*Annalen*, 1913, **401**, 189—232).—Since Morot in 1849, and Frémy and Cloëz in 1854, isolated in an impure state the blue pigment of the cornflower, very little work has been recorded, probably on account of the instability of the anthocyanin. An important observation by Molisch (*Bot. Zeit.*, 1905, **63**, 145), that in the flowers and red leaves of many plants the anthocyanin occurs, not merely in solution in the cell juice, but also in the crystal-

line or amorphous state, revived interest in the subject, and observations, many of which are erroneous, have been recorded by Grafe, by Glan, by Griffiths (A., 1904, i, 179), and by Combes (A., 1911, ii, 1125).

Anthocyanins are the blue, violet, and red pigments which are extracted from flowers, fruits, and many leaves by water or aqueous alcohol, and are insoluble in ether; they are roughly classified by their colour reactions in acid and in alkaline solution and with lead acetate. For the sake of completeness, it may be recalled that red and blue flowers also contain yellow pigments, anthoxanthins, which are soluble in water or dilute alcohol, and are quite different from the chemically indifferent carotine. The blue pigment of the cornflower is unstable and very difficult to isolate, and has not yet been obtained crystalline. The various shades of colour in different parts of the flower are due to various derivatives of one substance. Thus the blue pigment is the potassium salt of an acid (cyanin), the violet pigment is the free acid, and the red pigments are oxonium salts of cyanin and plant-acids. In addition, a colourless substance can be isolated from the flowers, which is an isomeride of cyanin and is acid and forms colourless alkali salts.

All anthocyanins are present in flowers as glucosides and not, as previously stated by Grafe, partly in combination with dextrose and partly not. They all exhibit a characteristic reaction, the anthocyanidin reaction; an anthocyanin dissolved in *N*- or 2*N*-sulphuric acid is quite unaffected by shaking with amyl alcohol, but after hydrolysis on the water-bath, the coloured fission product (anthocyanidin) is quantitatively extracted by the alcohol, forming a reddish-violet solution, which is changed to bluish-violet by washing, or more rapidly by sodium acetate. (In this connexion, Erdmann's test for new, or comparatively new, red wine is discussed.)

In order to isolate the colouring matter, dried cornflower meal, mixed with six parts of sand to facilitate filtration, is rapidly extracted with water or 20% alcohol, preferably in the presence of sodium nitrate or chloride to retard the change of the anthocyanin to the colourless modification. The deep blue solution is treated with alcohol and the potassium cyanin, after repeated fractional precipitation with water and alcohol, is obtained mixed with at least twice the weight of carbohydrates, albumins, and pentosans. In its further purification, the blue pigment is treated with alcohol and hydrochloric acid, whereby the pentosans (one of which is probably xylan) are precipitated, and the pigment is converted in *cyanin chloride*, $C_{28}H_{33}O_{17}Cl,3H_2O$, m. p. 203—204° (corr.) (anhydrous), dark blue, rhombic leaflets with golden reflex. The chloride is extremely hygroscopic, and forms stable red solutions in acids; its aqueous solution rapidly becomes colourless, but recovers its red colour by the addition of an acid. A solution of the chloride becomes violet in the presence of calcium carbonate, and changes from red through violet to cornflower blue by treatment with sodium carbonate.

By hydrolysis with boiling 20% hydrochloric acid for three to three and a half-minutes, cyanin chloride yields dextrose (2 mols.) and *cyanidin chloride*, $C_{16}H_{13}O_7Cl$, long, brownish-red, metallic needles,

which decomposes by slow heating, but has m. p. 220° (decomp.) when placed directly in a bath at this temperature. Like cyanin chloride, cyanidin chloride is converted by aqueous sodium carbonate, firstly, into a violet solution of the acid, cyanidin, and then into a blue solution of sodium cyanidin. Moreover, cyanidin chloride in dilute alcohol at 85° is slowly converted into an *isomeride*, colourless crystals, which is reconverted into red cyanidin salts by boiling dilute mineral acids; by prolonged keeping of its aqueous alcoholic or ethereal solution, the colourless isomeride changes to another *substance*, colourless needles, from which the red cyanidin salts cannot be regenerated.

Little can be stated at present with regard to the constitutions of cyanin and cyanidin. The fact, that the two substances form very stable salts with hydrochloric acid, indicates that cyanin and cyanidin are related to benzopyronium (Decker and Fellenberg, A., 1909, i, 116) rather than to the flavones. C. S.

Hydrogenation of a Secondary Alcohol derived from Furfuraldehyde in the Presence of Nickel. ROGER DOURIS (*Compt. rend.*, 1913, 157, 722—724).—During the catalytic hydrogenation of certain secondary α-ethylenic alcohols, dehydration occurs, followed by hydrogenation of the ethylenic hydrocarbon produced. The author is extending this study to heterocyclic alcohols derived from furfuraldehyde. Furfuraldehyde itself gives α-methylfuran, α-methyltetrahydrofuran, methyl propyl ketone, and pentan-β-ol (compare Padoa and Ponti, A., 1907, i, 146). Furylethylcarbinol on hydrogenation in the presence of reduced nickel at 175° yields propyltetrahydrofuran, dipropyl ketone, *ethyltetrahydrofurylcarbinol*, $C_4H_7O{\cdot}CHEt{\cdot}OH$, a colourless, syrupy liquid, b. p. 87—90°/15 mm., D_4^0 1·0051, D_4^{20} 0·9869, and a small quantity of a liquid, b. p. 110—120°/15 mm., which contains a glycol.

Whilst furylethylcarbinol, unlike its propyl and *iso*amyl homologues, will not yield an acetic ester, yet its tetrahydro-derivative readily yields an *ester*, a colourless liquid, b. p. 90—91°/12 mm., D_4^0 1·0334, D_4^{20} 1·0149. W. G.

Action of Fermenting Yeast on Furfuraldehyde. Formation of Furyltrimethylene Glycol. II. CARL J. LINTNER and H. J. VON LIEBIG (*Zeitsch. physiol. Chem.*, 1913, 88, 109—121. Compare A., 1911, ii, 816).—Furfuraldehyde in presence of yeast which is actively fermenting sucrose is converted into *furyltrimethylene glycol* [*αγ-dihydroxy-α-furylpropane*], $C_4H_3O{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}OH$. This crystallises in very tiny needles, m. p. 50·5°, $[\alpha]_D$ −10·5°; with concentrated sulphuric acid it gives a gentian-blue coloration.

The *diacetate* forms a pale yellow oil with an aromatic odour, b. p. 246—248°/720 mm.; the *dibenzoyl* derivative is likewise a pale yellow oil. Both compounds have a normal molecular weight and give a blue coloration with sulphuric acid.

The *di*-p-*nitrobenzoate* forms an almost colourless, crystalline powder, m. p. 150—151°. The *diphenylurethane*, which is a colourless, light powder, has m. p. 195°.

It is assumed that the acetaldehyde formed as the first product of the fermentation of dextrose undergoes an aldol condensation with furfuraldehyde and that this aldol is immediately reduced to the glycol by the yeast. E. F. A.

Thioflavones [2-Phenyl-1 : 4-benzothiopyrones]. SIEGFRIED RUHEMANN (*Ber.*, 1913, **46**, 3384—3395).—The sodium salts of the thiophenols, like the ordinary phenols (this vol., i, 891), can undergo condensation with ethyl phenylpropiolate with formation of the ethyl esters of the corresponding β-arylthiolcinnamic acids. The free acids on heating lose carbon dioxide with formation of arylthiolstyrenes, and by successive treatment with phosphorus pentachloride and aluminium chloride they are almost quantitatively converted into thioflavones (2-phenyl-1 : 4-benzothiopyrones). The last-named substances are more resistant than the flavones towards alkali, but by prolonged boiling with concentrated potassium hydroxide solution two concurrent decompositions are effected, one yielding (with thioflavone itself) benzoic acid and o-thiolacetophenone, and the other acetophenone and o-thiolbenzoic acid.

The corresponding 1 : 4-benzothiopyrone, $C_6H_4<\begin{matrix}CO\cdot CH\\ S—CH\end{matrix}$, could not be produced in a similar manner on account of the impossibility of hydrolysing ethyl phenylthiofumarate (obtainable from the sodium compound of the thiophenol and ethyl chlorofumarate) without complete decomposition.

Ethyl β-o-tolylthiolcinnamate, $C_6H_4Me\cdot S\cdot CPh\colon CH\cdot CO_2Et$, a viscous, yellow oil, b. p. 230°/12 mm., which slowly crystallises, is obtainable by the gradual addition of ethyl phenylpropiolate to a hot solution of sodium in excess of *o*-tolyl mercaptan diluted with toluene; *β-o-tolylthiolcinnamic acid*, produced by hydrolysis with alcoholic potassium hydroxide, forms colourless needles, m. p. 160—161° (decomp.), and on heating passes into *o-tolylthiolstyrene*, $C_6H_4Me\cdot S\cdot CPh\colon CH_2$, a yellow oil, b. p. 183—184°/12 mm., with loss of carbon dioxide. When powdered aluminium chloride is gradually introduced into a mixture of phosphorus pentachloride and β-o-tolylthiolcinnamic acid in benzene, intramolecular condensation to *2-phenyl-8-methyl-1 : 4-benzothiopyrone* (*8-methylthioflavone*), $C_6H_3Me<\begin{matrix}CO\cdot CH\\ S—CPh\end{matrix}$, pale yellow needles, m. p. 124—125°, is effected.

p-Tolyl mercaptan, obtained by reduction of *p*-toluenesulphonyl chloride, condenses in a similar manner to the ortho-isomeride, with ethyl phenylpropiolate, producing the *ethyl* ester, yellowish prisms, m. p. 77—78°, b. p. 240—242°/12 mm., of *β-p-tolylthiolcinnamic acid*, colourless needles, m. p. 167° (decomp.). By successive treatment with phosphorus pentachloride and aluminium chloride the acid is converted into *2-phenyl-6-methyl-1 : 4-benzothiopyrone* (*6-methylthioflavone*), colourless needles, m. p. 153—154°.

Thiol-*p*-xylene, b. p. 211—212°, obtained from the corresponding sulphinic acid, which was prepared by the diazo-reaction, condensed with ethyl phenylpropiolate, giving the viscous, yellow *ethyl* ester,

b. p. 242°/12 mm., of *β-p-xylylthiolcinnamic acid*, colourless prisms, m. p. 186—187° (decomp.). Treatment with phosphoric and aluminium chlorides converts this into *2-phenyl-5 : 8-dimethyl-1 : 4-benzothiopyrone* (*5 : 8-dimethylthioflavone*), $C_6H_2Me_2<\begin{array}{l}CO\cdot CH\\ S—CPh\end{array}$, colourless needles, m. p. 133—134°.

Thiol-*m*-xylene, b. p. 212—214°, in a similar manner, condenses with ethyl phenylpropiolate, giving the *ethyl* ester, yellow prisms, m. p. 91—92°, b. p. 242—244°/12 mm., of *β-m-xylylthiolcinnamic acid*, yellow prisms, m. p. 184° (decomp.). This acid, when heated, loses carbon dioxide with formation of *3 : 4-dimethylphenylthiolstyrene*, a yellow oil, b. p. 197—198°/14 mm., and under the usual treatment with phosphoric and aluminium chlorides gives rise to *2-phenyl-6 : 8-dimethyl-1 : 4-benzothiopyrone* (*6 : 8-dimethylthioflavone*), yellow needles, m. p. 152—153°.

o-Anisyl mercaptan, in the form of its sodium compound, reacts with ethyl phenylpropiolate in the general manner, giving the *ethyl* ester, colourless needles, m. p. 67—68°, b. p. 246—248°/12 mm., of *β-o-anisylthiolcinnamic acid*, colourless needles, m. p. 148° (decomp.). The acid is readily converted into *8-methoxy-2-phenyl-1 : 4-benzothiopyrone* (*8-methoxythioflavone*), $OMe\cdot C_6H_3<\begin{array}{l}CO\cdot CH\\ S—CPh\end{array}$, colourless needles, m. p. 129—130°. This compound, like the oxygen analogue (*loc. cit.*), can be demethylated by hydriodic acid, producing *8-hydroxy-2-phenyl-1 : 4-benzothiopyrone*, yellow prisms, m. p. 292° (decomp.).

The sodium compound of *p*-anisylmercaptan with ethyl phenylpropiolate produces the *ethyl* ester, b. p. 255—256°/14 mm., of *β-p-anisylthiolcinnamic acid*, colourless prisms, m. p. 217—218° (decomp.). This was transformed in the usual manner into *6-methoxy-2-phenyl-1 : 4-benzothiopyrone* (*6-methoxythioflavone*), colourless needles, m. p. 155—156°.

The behaviour of the benzothiopyrone compounds with alkali, towards which they are very stable, was especially investigated with 2-phenyl-1 : 4-benzothiopyrone (that is, thioflavone itself). It is completely changed by boiling with concentrated alcoholic sodium hydroxide for five to six hours; acetophenone, *o*-thiolacetophenone, as an oil oxidisable to dithiodiacetophenone $(C_6H_4Ac)_2S_2$, needles, m. p. 167—168° (compare Farbwerke Meister, Lucius, & Brüning, A., 1908, i, 987), benzoic acid, *o*-thiolbenzoic acid, and dithiodisalicylic acid could be recognised among the reaction products. D. F. T.

Aconitine Alkaloids. Pyraconitine. HEINRICH SCHULZE and A. LIEBNER (*Arch. Pharm.*, 1913, **251**, 453—467. Compare Schulze and Bierling, this vol., i, 287).—Pyraconitine, $C_{32}H_{43(or\ 41)}O_9N$ (Dunstan and Carr give $C_{31}H_{41}O_{10}N$; T., 1894, **65**, 176), prepared by heating aconitine at 192°, has m. p. 171°, $[\alpha]_D^{20}$ −112·2°, in 95% alcohol (c = 8·6918), and crystallises from ether in colourless needles containing $1\frac{1}{2}Et_2O$, and from alcohol in crystals containing $2\frac{1}{2}EtOH$. Dunstan and Read's pyrojapaconitin (T., 1900, **77**, 60), obtained by heating japaconitine at 192°, is identical with pyraconitine. The following

salts, prepared in all cases from both pyraconitine and "pyrojapaconitine," are described: hydrochloride, m. p. 167° (decomp.); aurichloride, m. p. 157—158° (decomp.): hydrobromide, m. p. 240—242° (decomp.) (hydrated) or 243—244° (decomp.) (anhydrous), $[\alpha]_D^{20}$ −105·87° in water ($c = 4·5339$); hydriodide, m. p. 157—158° (decomp.) (hydrated), and perchlorate, m. p. about 190°. The preceding constants differ from those recorded by Dunstan and Carr (*loc. cit.*). C. S.

*isoapo*Caffeine. Heinrich Biltz [with Paul Krebs and Karl Strufe] (*Ber.*, 1913, **46**, 3407—3410).—The substance *isoapo*caffeine, which is obtained together with *apo*caffeine in the oxidation of caffeine and 1 : 3 : 7-trimethyluric acid (Biltz and Krebs, A., 1910, i, 523), is 3 : 7-dimethylcaffolide; this has been demonstrated by a course of degradation detailed in this paper. The formation of *isoapo*caffeine from caffeine or trimethyluric acid must evidently be a fairly complex process which is partly synthetic; it is suggested that in addition to the direct oxidation to *apo*caffeine, some dimethylalloxan and methylcarbamide are produced, the latter substances then condensing to *isoapo*caffeine and *apo*caffeine. In support of this view it is mentioned that only when the oxidation is so moderated as to proceed slowly is any *isoapo*caffeine formed.

When an aqueous solution of *isoapo*caffeine is evaporated to a syrup, iso*caffuric acid*, $\begin{matrix}\text{NMe·CO}\\ \text{CO—NH}\end{matrix}\!>\!\text{C(OH)·CO·NHMe}$, is obtained, which gradually crystallises in prisms, m. p. 191° (decomp.).

When heated on a water-bath with hydriodic acid (D 1·96), *isoapo*caffeine undergoes reduction to 3-*methylhydantoin-5-carboxymethylamide*, $\begin{matrix}\text{NMe·CO}\\ \text{CO—NH}\end{matrix}\!>\!\text{CH·CO·NHMe}$, prisms, m. p. 240°. This substance is hydrolysed by barium hydroxide solution with formation of methylamine and 3-*methylhydantoin-5-carboxylic acid*, $\begin{matrix}\text{NMe·CO}\\ \text{CO—NH}\end{matrix}\!>\!\text{CH·CO}_2\text{H}$, tablets, m. p. 130° (decomp.); the latter, on gradually heating to 190°, eliminates carbon dioxide with production of 3-methylhydantoin, $\begin{matrix}\text{NMe·CO}\\ \text{C}\end{matrix}\!>\!\text{CH}_2$.

*isoapo*Caffeine consequently has the structure $\begin{matrix}\text{NMe·CO}\\ \text{CO—NH}\end{matrix}\!>\!\text{C}\!<\!\begin{matrix}\text{O—CO}\\ \text{CO·NMe}\end{matrix}$.

D. F. T.

Some New Salts of Quinine, Euquinine, Aristoquinine, Saloquinine, and Quinaphenine. Decio Angeloni (*Boll. chim. farm.*, 1913, **52**, 675—685).—A basic *salicylate* of *quinaphenine*, $C_{20}H_{23}O_2N_2$·CO·NH·C_6H_4·OEt,OH·C_6H_4·CO_2H, has m. p. 125—126°, and is obtained by adding an ethereal solution of the acid to an ethereal solution of an equimolecular quantity of the base. When 2 mols. of acid are taken and the base is poured into the acid, a salt, m. p. 112°, is obtained, which is, however, a mixture of the normal and basic salts.

When an ethereal solution of euquinine (1 mol.) is added to an ethereal solution of novaspirin ($\frac{1}{2}$ mol.), the normal *salt*, m. p. 95°, is obtained. By working in alcoholic solution, the basic *salt* may be prepared: it has m. p. 178°.

Novaspirin and aristoquinine yield the normal *salt*, m. p. 89—90°, in which the aristoquinine behaves as a tetracidic base. Novaspirin and saloquinine in ethereal solution yield the normal *salt*, m. p. 116°. Novaspirin and quinaphenine also yield the normal *salt*, m. p. 118—120°.

Diaspirin and quinine in ethereal solution yield the basic *salt*, which crystallises in needles, m. p. 125°. By taking an excess of acid, the normal *salt* may also be prepared. Diaspirin and quinaphenine in ethereal solution yield the normal *salt*, m. p. 116°.

Diplosal and quinine in ethereal solution yield the basic *salt*, m. p. 105°, which crystallises in needles. Diplosal and quinaphenine in ethereal solution also form the basic *salt*, m. p. 86°.

The compositions of the salts obtained were established by nitrogen estimations. Information is also given as to the solubilities of the bases and acids employed in ether. R. V. S.

The Apparent Colloidal Character and the Molecular Weight of Colchicine. SIMON ZEISEL and K. VON STOCKERT (*Monatsh.*, 1913, **34**, 1327—1338).—In aqueous solution, colchicine has many of the physical and physiological properties of a colloid. Diffusion experiments with a 20% solution show, however, that it is a crystalloid. The amyloid of the diffusion thimble has a great adsorptive power for the alkaloid, and until this is satisfied, the diffusion does not reach a normal value. Cryoscopic and ebullioscopic determinations of the molecular weight of colchicine, colchiceine, and trimethylcolchicinic acid in various solvents have also been made. In acetic acid or boiling ethylene dibromide, the results for colchicine agreed with the formula $C_{22}H_{25}O_6N$. In cold ethylene dibromide and especially in water, which is most unusual, bi- or even ter-molecular values were obtained. Colchiceine gave high values in freezing ethylene dibromide, and trimethylcolchicinic acid in boiling acetic acid.

J. C. W.

Bromine Derivatives of Colchicine. SIMON ZEISEL and K. VON STOCKERT (*Monatsh.*, 1913, **34**, 1339—1347).—When an excess of hydrobromic acid is added to a dilute solution of colchicine, sulphur-yellow *dibromocolchicine*, $C_{22}H_{23}O_6NBr_2$, is precipitated, m. p. 146—150° (open tube), 125° (sealed capillary). One molecular proportion of the acid precipitates the *monobromide*, which crystallises in various forms from methyl alcohol, but with constant properties,

$$C_{22}H_{24}O_6NBr,MeOH,$$

m. p. 151·5° (corr., open tube), 133—135° (sealed tube). It is somewhat soluble in water, and the addition of excess of hydrobromic acid to the aqueous mother liquors causes the precipitation of the above dibromide. In methyl alcohol solution, colchicine gives with excess of bromine in the cold, a *tribromide*, $C_{18}H_{10}(OMe)_4O_2NBr_3$, m. p. 131° (open), 118—122° (sealed). The behaviour of these derivatives

towards alkali hydroxides, in open vessels or in sealed tubes, shows that two bromine atoms are firmly combined, whilst the third is fairly labile. *Tribromocolchiceine*, $C_{21}H_{20}O_6NBr_3,H_2O$, and *tribromotrimethylcolchicinic acid*, $C_{19}H_{18}O_5NBr_3$, were also prepared. J. C. W.

Synthesis of Hygrine. I. KURT HESS (*Ber.*, 1913, **46**, 3113—3125).—Hygrine should have either the constitution I or II.

$$\text{(I) } CH_2{<}\begin{matrix}CH_2\cdot NMe\\ \vert\\ CH_2\cdot CH\cdot COEt\end{matrix} \qquad \text{(II) } CH_2{<}\begin{matrix}CH_2\cdot NMe\\ \vert\\ CH_2\cdot CH\cdot CH_2\cdot COMe\end{matrix}$$

Willstätter (A., 1900, i, 405) suggested that the second formula was probable, assuming, therefore, that hygrine and tropinone are somewhat similarly constituted, but the fact that the oxidation product, hygric acid (Liebermann and Cyhulski, A., 1895, i, 310; Willstätter, *loc. cit.*, and A., 1903, i, 362), is not an acetic acid derivative akin to tropic acid supports formula I. The author has attempted to synthesise the above isomerides, and has so far succeeded in preparing the corresponding hydroxy-compounds:

$$\text{(III) } CH_2{<}\begin{matrix}CH_2\cdot NMe\\ \vert\\ CH_2\cdot CH\cdot CHEt\cdot OH\end{matrix} \qquad \text{(IV) } CH_2{<}\begin{matrix}CH_2\cdot NMe\\ \vert\\ CH_2\cdot CH\cdot CH_2\cdot CHMe\cdot OH\end{matrix}$$

The former compound was obtained by treating magnesium pyrryl bromide with propionyl chloride, reducing the 2-propionylpyrrole so obtained by sodium and alcohol, and methylating the product. The other compound was prepared by the addition of propylene oxide to magnesium pyrryl bromide, reduction of the *iso*propyl alcohol derivative by means of hydrogen in presence of spongy platinum, and methylation of the pyrrolidyl-2-*iso*propyl alcohol.

a-2-Pyrrylpropan-β-ol, $C_4H_4N\cdot CH_2\cdot CHMe\cdot OH$, is a colourless, odourless, viscous oil, b. p. 94—96°/0·25 mm., which changes into a thick, red syrup in the air, and is soluble in water. No picrate nor oxidation product could be isolated, but it yielded 2-propylpyrrole (Dennstedt and Zimmermann, A., 1893, i, 226) on reduction with red phosphorus and hydriodic acid. It was accompanied by an isomeride, probably, $CH{<}\begin{matrix}CH\cdot NH\\ \vert\\ CH{:}C\cdot CHMe\cdot CH_2\cdot OH\end{matrix}$, which had b. p. 99—107°/0·25 mm.

For the methylation, it was found necessary to prepare the potassium compound and then to add methyl iodide. *a-1-Methylpyrrylpropan-β-ol*, $C_8H_{13}ON$, is a pleasant smelling oil, b. p. 116—117°/18 mm. The reduction of pyrrylpropan-β-ol with hydrogen in presence of platinum was successful when the necessity of excluding all traces of oxygen was realised. For this purpose an apparatus is described which consists essentially of a cylinder and bulb connected by a tap, the cylinder being also fitted with an inlet tube and a ground-on cap. The suspension of platinum in glacial acetic acid was saturated with hydrogen in the bulb, the solution of the alcohol was then washed with hydrogen in the cylinder, and finally the two liquids were shaken together under a slightly increased pressure. The platinum was not added all at once, but fresh portions were occasionally saturated with hydrogen in the cylinder and then allowed to flow into the bulb. The process required a few days. In

this way the formation of pyrrole dyes by catalytic oxidation was entirely prevented, and only a small quantity of platinum was required. A quantitative reduction of pyrrole itself, without the occurrence of a coloured solution, was also effected (compare Willstätter and Hatt, A., 1912, i, 545). *a-2-Pyrrolidylpropan-β-ol*, $C_4H_8N{\cdot}CH_2{\cdot}CHMe{\cdot}OH$, is a viscous oil, b. p. 115—120°/15 mm., with the usual properties of a base and an unsaturated compound. On methylation with methyl iodide and potassium hydroxide, a moderate yield of *a 1-methylpyrrolidylpropan-β-ol* (IV) was obtained as an oil, b. p. 98—103°/16 mm.

2-Pyrrylpropane-βγ-diol (future communication) was also reduced as above, yielding *a-2-pyrrolidylpropane-βγ-diol*

$$C_4H_8N{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH,$$

b. p. 145—150°/18 mm., which formed a very hygroscopic potassium salt.

The reduction of the isomeric alcohols was first studied in the case of 2-acetylpyrrole. Sodium was added to the boiling alcoholic solution of the substance and *a-2-pyrrolidylethan-a-ol (pyrrolidyl-2-methylcarbinol)*, $C_4H_8N{\cdot}CHMe{\cdot}OH$, was extracted from the product as a colourless oil, b. p. 187—192°/759 mm. It smells like acetamide and absorbs moisture and carbon dioxide with avidity. *a-2-Pyrrolidylpropan-a-ol (pyrrolidyl-2-ethylcarbinol)*, $C_4H_8N{\cdot}CHEt{\cdot}OH$, was prepared in this way from 2-propionylpyrrole. It is a well-defined, crystalline base, m. p. 50°, b. p. 95—98°/17 mm., 195—200°/756 mm., with a narcotic odour, is hygroscopic, and gives the Liebermann reaction. *a-1-Methylpyrrolidylpropan-a-ol (1-methylpyrrolidyl-2-ethylcarbinol)* (III.) is also a very hygroscopic base, m. p. 45°, b. p. 92—95°/17 mm., 190—195°/757 mm. J. C. W.

Origin of the Cyclic Bases of Coal-tar. LOUIS C. MAILLARD (*Compt. rend.*, 1913, **157**, 850—852).—The humic substances obtained by the condensation of sugars with different amino-acids (compare A., 1912, i, 169) readily yield cyclic bases when heated. The author applies this to the formation of coal from the constituents of cellulose and proteins and to its distillation, yielding coal-tar containing pyridine and other cyclic bases. W. G.

Allylpyrroles. KURT HESS (*Ber.*, 1913, **46**, 3125—3129).—When magnesium pyrryl bromide is treated with allyl bromide, a mixture of approximately equal quantities of 2-allyl- and 2 : 5-diallyl-pyrroles is obtained. The formation of the latter compound is explained by assuming that some magnesium pyrryl bromide reacts with 2-allylpyrrole, forming pyrrole and 5-magnesium-2-allylpyrryl bromide, which then unites with more allyl bromide. This view is supported by the fact that carbon dioxide converts the reaction product of 2-allylpyrrole and magnesium pyrryl bromide into 2-allylpyrryl-5-carboxylic acid, acid, from which it follows that allylpyrrole is more acidic than pyrrole.

The reaction between allyl bromide and magnesium pyrryl bromide

was vigorous but was not moderated by cooling. After steam distillation and extraction with ether, 2-*allylpyrrole*,

$$CH\Big\langle{CH\cdot NH \atop CH:\overset{|}{C}\cdot CH_2\cdot CH:CH_2},$$

was obtained as a colourless, mobile liquid, b. p. 82—83°/24 mm., D_4^{24} 0·9376. It has an unpleasant odour, rapidly becomes yellow in the air, finally forming a red, amorphous mass, and is extremely sensitive towards reagents. 2:5-Diallylpyrrole, $C_4H_3N(CH_2\cdot CH:CH_2)_2$, is a similar liquid, b. p. 110—115°/17 mm., D_4^{24} 0·9321. The addition of allylpyrrole to magnesium pyrryl bromide caused a change in colour from grey to dark green. After treatment with dry carbon dioxide, 2-*allylpyrrylcarboxylic acid*, $CH\Big\langle{C(CO_2H)\cdot NH \atop CH\!=\!=\!=\!\overset{|}{C}\cdot CH_2\cdot CH:CH_2}$, was obtained in indefinite crystals, m. p. 117—118°. It is unstable, and partly decomposes into violet-pink dyes even when boiled with light petroleum. J. C. W.

Equilibrium in the System Cobalt Chloride and Pyridine. J. NEWTON PEARCE and T. E. MOORE (*Amer. Chem. J.*, 1913, 50, 218—231).—In order to investigate the formation of compounds of cobalt chloride with pyridine of crystallisation, a study has been made of this system by the solubility method at temperatures between −50·3° and 100°. The results show the existence of three distinct crystalline compounds, $CoCl_2,2C_5H_5N$; $CoCl_2,4C_5H_5N$, and $CoCl_2,6C_5H_5N$. The first two of these have been isolated previously by Reitzenstein (A., 1895, i, 121). The compound $CoCl_2,2C_5H_5N$ has m. p. 195—200°, but the m. p.'s of the other two compounds cannot be ascertained, as they rapidly lose pyridine when heated under the ordinary pressure.

The compound $CoCl_2,6C_5H_5N$ exists as the solid phase between −50·3° and 15°, $CoCl_2,4C_5H_5N$ between 15° and 70°, $CoCl_2,2C_5H_5N$ between 70° and 90°, whilst between 90° and the b. p. of the saturated solution $CoCl_2$ is the stable, solid phase.

The usual methods of estimating cobalt are not satisfactory in presence of pyridine, and the following method was therefore devised. The weighed sample of solution was heated at 120° until all the pyridine had been removed. It was then dissolved in 50% alcohol, and an excess of oxalic acid was added to the solution. The precipitated cobalt oxalate was washed with 50% alcohol, dried at 100°, and dissolved in sulphuric acid (1:3). The solution was diluted to 300 c.c., heated nearly to boiling, and titrated with potassium permanganate. This method was found to be very accurate. E. G.

Cyclic Imines. VIII. Ring Opening in Substituted Indoles and Quinolines. JULIUS VON BRAUN, ALFRED GRABOWSKI, and MARGARETE RAWICZ (*Ber.*, 1913, **46**, 3169—3182).—A number of cyclic imines (substituted quinoline and indole derivatives) have been converted into compounds of the phenylpropane series primarily to determine with what yield the chlorinated amides could be obtained on treating the *N*-benzoyl compounds of the imines with phosphorus pentachloride, and to study the hydrolysis of these amides to the

chlorinated bases. It appears that the substituted anilides are formed even more readily than the unsubstituted compounds previously described, and they are readily purified from unchanged imine. They are hydrolysed with difficulty as the temperatures necessary to ensure hydrolysis and at which decomposition begins lie very near together.

6-*Chlorotetrahydroquinoline*, $C_6H_3Cl<\begin{matrix}CH_2\cdot CH_2\\ NH-CH_2\end{matrix}$, obtained by reduction of 6-chloroquinoline and isolated by means of the benzoyl compound, has b. p. 160°/11 mm., m. p. 43°. The *hydrochloride* crystallises in lustrous needles, m. p. 190°; the *platinichloride* is yellow, m. p. 185°. The *benzoyl* derivative has m. p. 84°. The *picrate*, m. p. 151°, and the *nitroso*-compound, m. p. 65°, are also described.

On heating the benzoyl derivative with phosphorus pentachloride at 140°, *benzo-p-γ-dichloro-o-propylanilide*,

$$CH_2Cl\cdot CH_2\cdot CH_2\cdot C_6H_3Cl\cdot NH\cdot COPh,$$

is obtained in a mass of snow-white crystals, m. p. 108°. On prolonged heating with concentrated hydrochloric acid at 125°, p-γ-*dichloro-o-propylaniline hydrochloride* is obtained, m. p. 170°. The free base, $C_3H_6Cl\cdot C_6H_3Cl\cdot NH_2$, is a slightly coloured, almost odourless oil. The yellow *platinichloride*, has m. p. 181—182°, and the *picrate* has m. p. 143°.

On diazotisation and treatment with cuprous chloride, 2 : 5-γ-*trichloropropylbenzene*, $C_6H_3Cl_2\cdot C_3H_6Cl$, is obtained as a colourless oil of agreeable odour, b. p. 152°/16 mm.

7-*Nitrotetrahydroquinoline*, $NO_2\cdot C_6H_3<\begin{matrix}CH_2\cdot CH_2\\ NH\cdot CH_2\end{matrix}$, prepared by nitrating tetrahydroquinoline in concentrated sulphuric acid, forms a yellowish-red, crystalline mass, m. p. 90°. The *hydrochloride* separates in colourless needles, m. p. 203°; the colourless *benzoyl* derivative has m. p. 141°, whereas the *nitroso*-compound has m. p. 118—120°.

On opening the ring with phosphorus pentachloride, *benzo-γ-chloro-5-nitro-2-propylanilide*, $C_3H_6Cl\cdot C_6H_3(NO_2)\cdot NHBz$, is obtained in well formed, colourless needles, which are converted on hydrolysis at 120° into γ-*chloro-5-nitro-2-propylaniline*, a red compound, m. p. 76°. The *hydrochloride* has m. p. 217°, the *platinichloride* forming a yellow, crystalline precipitate.

Heating with dimethylamine converts the benzonitroanilide into *benzo-γ-dimethylamino-5-nitro-2-propylanilide*,

$$NMe_2\cdot C_3H_6\cdot C_6H_3(NO_2)\cdot NHBz,$$

crystallising in well formed, colourless needles, m. p. 157°. The *hydrochloride* and *picrate* are oily.

γ-*Dimethylamino-5-nitro-2-propylaniline*, obtained on hydrolysis, separates in yellow crystals, m. p. 65—66°. The *dihydrochloride* has m. p. 191°, and the *dipicrate*, m. p. 146°.

6-*Chloro-7-nitrotetrahydroquinoline* forms red crystals, m. p. 84°. The *hydrochloride*, m. p. 184°, becomes red in presence of moisture. The yellow *nitroso*-derivative has m. p. 124°, and the *benzoyl* derivative has m. p. 126°.

Dichlorobenzo-4-γ-dichloro-5-nitro-2-propylanilide is colourless, m. p. 173—174°. Hydrolysed at 120—125° it forms 4-γ-*dichloro-5-nitro-2-*

propylaniline: this is yellow, m. p. 90°, and forms a colourless *hydrochloride*, m. p. 150—151°, which becomes bright yellow when wet.

7-*Benzoylaminotetrahydroquinoline*, m. p. 189°, forms a *platinichloride*, m. p. 280—282°.

7-*Aminotetrahydroquinoline*, obtained either on hydrolysis of the above or by reducing the corresponding nitro-compound, forms a colourless oil, b. p. 195°/15 mm., m. p. 60°. The *hydrochloride*, m. p. 240°, and the *dibenzoyl* derivative, m. p. 233°, are described. The 2 : 3-*dibenzoylamino-γ-chloropropylbenzene*,

$$C_3H_6Cl\cdot C_6H_3(NHBz)_2,$$

obtained from this has m. p. 198—200°, forming a colourless powder.

The *acetyl* derivative, $NHAc\cdot C_6H_3<\begin{matrix}CH_2-CH_2\\ NMe\cdot CH_2\end{matrix}$, of 7-aminokairoline, m. p. 114°, when treated with cyanogen bromide forms 1-*cyano-7-acetylaminotetrahydroquinoline*, m. p. 152°, which is hydrolysed to 7-*aminotetrahydroquinoline*, m. p. 60°.

6-*Nitrodihydroscatole*, $NO_2\cdot C_6H_3<\begin{matrix}CHMe\\ NH\end{matrix}>CH_2$, from dihydroscatole, has m. p. 75°; the *hydrochloride* has m. p. 192°, the yellow *nitroso*-compound has m. p. 100°, and the *benzoyl* derivative, which crystallises in lustrous platelets, has m. p. 148°. *Benzo-5-nitro-2-β-chloroisopropylanilide*, $NHBz\cdot C_6H_3(NO_2)\cdot CHMe\cdot CH_2Cl$, crystallises in colourless, matted needles, m. p. 110°. Hydrolysis at 125° converts it into *nitrodihydroscatole hydrochloride*, m. p. 192°.

6-*Nitrodihydromethylindole*, $NO_2\cdot C_6H_3<\begin{matrix}CH_2\\ NH\end{matrix}>CHMe$, has m. p. 50°, and forms a *benzoyl* compound, m. p. 137°, a *hydrochloride*, m. p. 200° after sintering previously, and a nitroso-compound, m. p. 103—104°. *Benzo-5-nitro-2-β-chloropropylanilide*,

$$PhCO\cdot NH\cdot C_6H_3(NO_2)\cdot CH_2\cdot CHMeCl,$$

is colourless, m. p. 150°, and is converted on hydrolysis into 5-*nitro-2-β-chloropropylaniline*, a yellowish-red, crystalline mass, m. p. 84°. Treatment with dimethylamine converts it into 2-*β-benzo-5-nitro-2-dimethylaminopropylanilide*, $NO_2\cdot C_6H_3(NHBz)\cdot CH_2\cdot CHMe\cdot NMe_2$, crystallising in colourless needles, m. p. 122°. The analogous *piperidino*-compound, $NO_2\cdot C_6H_3(NHBz)\cdot CH_2\cdot CHMe\cdot NC_5H_{10}$, has m. p. 117°. E. F. A.

Action of Phosphoric Oxide on Benzylideneacetoneoxime. H. Burstin (*Monatsh.*, 1913, **34**, 1443—1448).—Goldschmidt (A., 1895, i, 392) by warming benzylideneacetoneoxime with phosphoric oxide could only isolate *iso*quinoline, whereas 2-methylquinoline or 1-methyl*iso*quinoline would represent a normal course for the condensation. The author has obtained a similar product, b. p. 240—250°, which gave a platinichloride, and corresponded with a mixture of the homologous quinolines. By the formation of quinophthalone (Jacobsen and Reimer, A., 1883, i, 812) and quinoline-2-carboxylic acid (Koenigs, A., 1899, i, 390), the presence of 2-methylquinoline was proved, whilst the formation of *iso*quinoline-red (Vongerichten and Homann, this vol., i, 99) indicated the presence of a mixture of 2-methylquinone and *iso*quinoline. J. C. W.

Condensation of Phenyl*iso*oxazolone with Ethyl Mesoxalate. ANDRÉ MEYER (*Bull. Soc. chim.*, 1913, [iv], 13, 903—909).—By the condensation of these two products it was expected that coloured substances of the general formula $\begin{matrix}\text{N:CPh} \\ | \\ \text{O—CO}\end{matrix}\!\!>\!\text{C:C(CO·R)·CO}_2\text{R}'$ would be produced, but instead it was found that two molecules of phenyl*iso*oxazolone took part in the reaction with the formation of compounds of the type $\begin{matrix}\text{N:CPh} \\ | \\ \text{O—CO}\end{matrix}\!\!>\!\text{CH·C(CO}_2\text{R)}_2\text{·CH}\!<\!\!\begin{matrix}\text{CPh:N} \\ | \\ \text{CO—O}\end{matrix}$, or their enolic forms.

*Ethyl mesoxalate bisphenyl*isooxazolone [*Bis-3-phenyl*isooxazolone-4-*malonate*], m. p. 187° (decomp.), forms large octahedra by slow evaporation of its solutions or small, prismatic crystals from acetic acid or boiling alcohol; it is soluble in alkalis and can be titrated, 1 mol. requiring 2 mols. of alkali to produce neutrality in presence of phenolphthalein. The sodium *salt* is crystalline and hygroscopic; those of the heavy metals are colourless and amorphous; ferric chloride gives a violet precipitate.

The sodium salt with ethyl iodide furnishes the *diethyl ether*, m. p. 200—201°, crystallising in silky, slender needles. The *diacetyl* derivative, m. p. 165—166°, forms small, prismatic crystals, and the *dibenzoyl* derivative, m. p. 194°, colourless leaflets or stellate groups of prismatic needles. Cryoscopic determinations of the molecular weight of the latter gave abnormal results. With benzenediazonium chloride, ethyl bis-3-phenyl*iso*oxazolone-4-malonate gave benzeneazophenyl*iso*oxazolone. T. A. H.

The Constitution of Dinitrothiodiphenylamine [Dinitrophenthiazine]. FRIEDRICH KEHRMANN and FERD. RINGER (*Ber.*, 1913, 46, 3014—3020. Compare Möhlau, Beyschlag, and Köhres, A., 1912, i, 212).—The authors believe that the dinitrophenthiazine obtained by Möhlau and his collaborators (*loc. cit.*) by the condensation of picryl chloride with *o*-benzoylaminophenyl mercaptan and subsequent treatment with sodium hydroxide solution is actually identical with and not an isomeride of the 3 : 5-dinitrophenthiazine described by Kehrmann and Schild (A., 1900, i, 61). In spite of the presence of the benzoyl radicle, the picryl chloride must therefore have made the amino-group and not the mercaptan group its main point of attack. In the action of picryl chloride on free aminophenyl mercaptan as well as on its benzoyl derivative, however, by-products are obtained which probably represent the isomerides of the main products and have the picryl radicle attached at the sulphur atom.

The compound, golden-yellow prisms, m. p. 169°, which is the main product of the interaction of picryl chloride and *o*-benzoylaminophenyl mercaptan, is therefore considered to have the structure

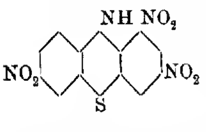
$$SH·C_6H_4·NBz·C_6H_2(NO_2)_3,$$

that is, *benzo-2 : 4 : 6-trinitro-2′-thioldiphenylamide*, whilst the substance, orange-yellow, leafy crystals, m. p. 142°, which results in smaller quantity, is probably the true trinitrophenyl *o*-benzoylaminophenyl sulphide. If the former substance, m. p. 169°, dissolved in alcohol is

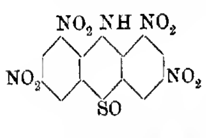
treated with dilute sodium hydroxide solution and left at the ordinary temperature, there slowly separates 3 : 5-*dinitro*-6-*benzoylphenthiazine*, $C_6H_4<\substack{NBz \\ S}>C_6H_2(NO_2)_2$, straw-yellow leaflets, m. p. 209°, which on hydrolysis by alcoholic sodium hydroxide undergoes conversion into 3 : 5-dinitrophenthiazine, m. p. 188—190°, identical with the product of Kehrmann and Steinberg (A., 1911, i, 1034); the m. p. 218°, observed by Möhlau and his collaborators, must be due either to the occurrence of dimorphism or to the presence of impurities.

The substance described by Möhlau as 2 : 4-diaminophenazthionium ferrichloride (*loc. cit.*) is in reality the ferrichloride of 3 : 5-diaminophenazthionium, the experimental conditions deciding whether the ferrichloride or merely the chloride (Kehrmann and Schild, *loc. cit.*) shall separate.

When a suspension of 3 : 5-dinitrophenthiazine in cold acetic acid is gradually treated with powdered sodium nitrite (compare this vol., i, 1231), the substance passes into solution and there separates 3 : 5 : 9-*trinitrophenthiazine* (annexed formula), brownish-red, lustrous prisms, m. p. 214°. This substance by reduction in alcoholic solution by stannous chloride and hydrochloric acid, followed by oxidation of the separated, colourless *zincochloride* with ferric chloride, passes into 3 : 5 : 9-*trinitrophenazthionium chloride*, long needles with a metallic green lustre; *nitrate*, sparingly soluble; *platinichloride*, violet-black, crystalline powder.



The identity of the dinitrophenthiazine resulting from the methods of the two above-mentioned groups of investigators was further confirmed by energetic nitration, when 3 : 5 : 7 : 9-tetranitrodiphenylaminosulphoxide (annexed formula) was obtained in each case as well as in the nitration of 3 : 9-dinitro- and of 3 : 5 : 9-trinitro-phenthiazine.



A closer examination of the reaction product from *o*-aminophenyl mercaptan and picryl chloride reveals the presence of a small quantity of a *substance*, straw-yellow tablets, in addition to the 2 : 4 : 6-trinitro-2′-thioldiphenylamine which was described earlier. It is believed that the former is possibly trinitrophenyl aminophenyl sulphide. D. F. T.

Preparation of *N*-Alkyl-*p*-phenylenediaminesulphonic Acids CHEMISCHE FABRIKEN VORM. WEILER-TER MEER (D.R.-P. 264927).—*N*-Alkyl-*p*-phenylenediaminesulphonic acids are obtained by the action of neutral alkali sulphites on *p*-nitroso-compounds of secondary or tertiary amines of general formula $NO{\cdot}R{\cdot}NR_1R_2$, where R is phenyl or a homologue of the same, R_1 hydrogen, alkyl or alkylaryl, and R_2 alkyl or alkylaryl.

p-*Phenylene*-as-*dimethyldiaminesulphonic acid*, $C_8H_{12}O_3N_2S$ (in which the sulphonic group is probably ortho- to the primary amino-group), is obtained when an aqueous solution of *p*-nitrosodimethylaniline (10 parts) is slowly treated at the ordinary temperature with a solution

of sodium sulphite (30 parts), and when the nitroso-compound has completely dissolved the mixture boiled with concentrated hydrochloric acid (90 parts); the acid is extremely soluble in water, but can be purified and finally isolated by means of its crystalline *benzylidene* derivative.

p-*Phenylene*-as-*diethyldiaminesulphonic acid* (prepared from nitrosodiethylaniline) is more readily isolated in crystalline form, whilst p-*phenylene*-as-*benzylethyldiaminesulphonic acid* furnishes a sparingly soluble *sodium* salt.

o-*Tolylene*-2-*ethyldiaminesulphonic acid* is obtained in a similar manner from *p*-nitrosoethyl-*o*-toluidine, and is isolated through its *benzylidene* derivative. F. M. G. M.

Leuco-bases and Colouring Matters Derived from Diphenylethylene. VI. The First Stage in the Oxidation of the *cyclo*Hexylidene Leuco-base, $C_6H_{10}:C[C_6H_4 \cdot NMe_2]_2$. Tetrahydromalachite-green. PAUL LEMOULT (*Compt. rend.*, 1913, **157**, 597—599. Compare A., 1912, i, 791).—Tetramethyldiaminodiphenyl*cyclo*hexylidenemethane (formula I), when acted on by lead peroxide, gives a bluish-coloured substance, which spontaneously decomposes in aqueous solution, giving the compound (formula III) having two atoms of hydrogen less than the initial leuco-base (compare *loc. cit.*):

$$\text{(I.)}\ CH_2{<}{CH_2 \cdot CH_2 \atop CH_2 \cdot CH_2}{>}C:C(C_6H_4 \cdot NMe_2)_2$$

$$\text{(II.)}\ C_6H_9 \cdot C(OH)(C_6H_4 \cdot NMe_2)_2 \qquad \text{(III.)}\ C_6H_8:C(C_6H_4 \cdot NMe_2)_2.$$

The author has now succeeded in isolating the unstable substance (formula II) by precipitating it from acid solution with ammonia, drying it in a vacuum over sulphuric acid, followed by crystallisation from benzene. Heated slowly, it has m. p. 130—135°, heated rapidly, m. p. 160°, whilst the instantaneous m. p. is 145°. If the liquid is allowed to cool and re-melted it has m. p. 165°, which is in accord with elimination of water, giving substance III, m. p. 169° (*loc. cit.*). This transformation is also brought about by simple crystallisation from hot alcohol.

The oxygenated compound on solution in cold alcohol to which one drop of acetic acid has been added, gives a persistent, deep blue solution, thus differing from substances I and II, and in slightly acid solution it dyes cotton, mordanted with tannin, a tint comparable to that given by malachite-green, but appreciably bluer. The absorption spectra of these two compounds, however, show marked differences.

W. G.

Leuco-bases and Colouring Matters of Diphenylethylene. VII. Action of Magnesium Methyl and Ethyl Iodides on Michler's Ketone. PAUL LEMOULT (*Compt. rend.*, 1913, **157**, 724—726).—A repetition of Fecht's experiments on the action of magnesium methyl and ethyl iodides on Michler's ketone (compare A., 1907, i, 926). Contrary to Fecht's statements, but in agreement with the results of Freund and Mayer (compare A., 1906, i, 384), the author obtained no carbinols of the type $OH \cdot CMe(C_6H_4 \cdot NMe_2)_2$, but a mixture of substances from which he separated unchanged ketone,

an ethylenic derivative of the type $CH_2:C(C_6H_4 \cdot NMe_2)_2$, and in the case of magnesium methyl iodide, small quantities of a substance crystallising in yellow needles, m. p. 157—158°, having the composition $C_{18}H_{22}N_2$, but a molecular weight corresponding to twice this, together with two other basic substances, crystallising (*a*) in yellow plates, m. p. 227°, and (*b*) in yellow crystals, m. p. 274°, the constitutions of which have not yet been determined. In the case of magnesium ethyl iodide, no substances corresponding with the last three were found, but a 90% yield of the ethylenic compound, $CHMe:C(C_6H_4 \cdot NMe_2)_2$, was obtained. W. G.

Ditertiary Hydrazines. XVI. Mechanism of the Blue Colour Reaction of Diphenylamine. HEINRICH WIELAND [with CARL MÜLLER] (*Ber.*, 1913, **46**, 3296—3303).—The blue coloration formed in sulphuric acid solutions of diphenylamine by oxidising agents was considered to be an acid sulphate of diphenyl dihydrophenazonium. Kohrmann and Micewicz (A., 1912, i, 1020) have shown that it is more probably a quinonoid derivative of diphenylbenzidine, $PhN:C_6H_4:C_6H_4:NHPh \cdot O \cdot SO_3H$. This explanation is now accepted, although it is not applicable to the colour reactions obtained with diphenylhydrazine, diphenylhydroxylamine, and *p*-dianisylamine.

Diphenylamine in dilute sulphuric acid and acetic acid solution is readily oxidised to the blue dye, which is easily reduced without the formation of by-products to diphenylbenzidine. Tetramethylhydrazine gives only small quantities of diphenylbenzidine as well as amorphous products; its formation cannot, therefore, be regarded as an intermediate stage in the colour reaction.

Triphenylamine shows a similar blue coloration on oxidation, when quinonoid salts of tetraphenylbenzidine are formed. *Tetraphenylbenzidine* crystallises in pale yellow needles, m. p. 226°, to a brownish-yellow liquid.

s-*Diphenyl*-o-*phenylenediamine*, $C_6H_4(NHPh)_2$, obtained by the action of iodobenzene and copper powder on *o*-aminodiphenylamine, crystallises as colourless double pyramids, m. p. 152·5°. On attempting to combine it with *o*-dibromobenzene to diphenyldihydrophenazine, only amorphous products were obtained. E. F. A.

Ditertiary Hydrazines. XVII. Diphenylhydroxylamine and Some Colour Reactions Related to the Blue Diphenylamine Reaction. HEINRICH WIELAND and CARL MÜLLER (*Ber.*, 1913, **46**, 3304—3314).—Diphenylhydroxylamine reacts with 75% sulphuric acid to form 70% of diphenylbenzidine, together with a little diphenylamine and a green dye of high molecular complexity. The quinonoid-blue salt is formed in this instance by direct elimination of water from diphenylhydroxylamine. When the sulphuric acid is diluted with acetic acid instead of water, the anhydro-product obtained is carbazole together with considerable quantities of *p*-hydroxydiphenylamine.

Even ice-cold sulphuric acid converts diphenylhydrazine into diphenylhydroxylamine, which is converted into diphenylbenzidine

as described. Much ammonia is also formed, also traces of *o*-aminodiphenylamine and some *p*-hydroxydiphenylamine.

p-Tolylhydrazine and concentrated sulphuric acid give at first a bluish-green and green coloration due to hydroxylamine, and ammonia is also formed. Further decomposition yields a yellowish-brown, amorphous substance and much ditolylamine.

Tetraphenyl- and *p*-tetratolyl-hydrazine dissolve in sulphuric acid with a reddish-violet coloration which changes to blue. Diphenylamine and ditolylamine are also formed respectively.

On oxidation of *p*-dianisylamine with persulphate and sulphuric acid, the salt, $OMe\cdot C_6H_4\cdot N:C_6H_4:OMe\cdot O\cdot SO_3H$, is first formed, but could not be isolated. A blue sulphate of the character of an indophenol which is red in solution was obtained; it very readily yields *p*-benzoquinone on treatment with dilute acids, and is considered to be the acid sulphate of a polymerised bimolecular *anisylquinone monoimine*,

$$HO\cdot C_6H_4\cdot N(C_6H_4\cdot OMe)\cdot C_6H_3(OMe)\cdot N:C_6H_4O.$$

E. F. A.

The Action of Organomagnesium Compounds on Diazomethane and Ethyl Diazoacetate. II. ERNST ZERNER (*Monatsh.*, 1913, 34, 1631—1638. Compare this vol., i, 1312).—The author makes some observations on the paper by Forster and Cardwell (T., 1913, **103**, 86) on the constitution of aliphatic diazo-compounds, and describes the preparation of benzaldehydephenylhydrazone by the action of diazomethane on magnesium phenyl bromide. The formation of this compound is assumed to follow the course:

$$CH_2:N\cdot N + PhMgBr \longrightarrow CH_2:N\cdot NPh\cdot MgBr + PhMgBr \longrightarrow$$
$$CH_2Ph\cdot NMgBr\cdot NPh\cdot MgBr \longrightarrow CH_2Ph\cdot NH\cdot NH\cdot CH_2Ph \longrightarrow$$
$$CHPh:N\cdot NHPh.$$

The ring formula for the fatty diazo-compound would require that at least one nitrogen atom would be involved in the addition of two molecules of the magnesium compound, which is contrary to experience.

J. C. W.

The Condensation of Ethyl Oxalate with Pyrazolones. WILHELM WISLICENUS, HEINRICH ELVERT, and PAUL KURTZ (*Ber.*, 1913, 46, 3395—3407).—On the addition of a benzene solution of phenylmethylpyrazolone (prepared from ethyl acetoacetate) to a mixture of ethyl oxalate and potassium ethoxide dissolved in ether, there separates slowly the *potassium* derivative, yellowish-white crystals, decomp. between 138° and 145°, of *ethyl* 1-*phenyl*-3-*methyl*-5-*pyrazolone*-4-*glyoxylate*, $CO_2Et\cdot CO\cdot CH<\begin{matrix}CO-NPh\\ CMe\cdot \overset{|}{N}\end{matrix}$, yellowish-white needles, m. p. 81—82°, which can be liberated by addition to cold dilute hydrochloric acid; the ester gives a deep red coloration with ferric chloride and also with common benzene and sulphuric acid; its tendency to enolisation is further evidenced by the formation of a green *copper* derivative, m. p. 220—223°, and of an *ammonium* derivative, m. p. 120—123° (decomp.). Treatment of the ester with phenylcarbimide caused the formation of the *carbanilate* of *ethyl* 1-*phenyl*-3-*methyl*-5-*pyrazolol*-4-*gly*-

oxylate, $N\begin{matrix}\diagup NPh-C\cdot O\cdot CO\cdot NHPh \\ \diagdown CMe-\overset{||}{C}\cdot CO\cdot CO_2Et\end{matrix}$, colourless needles, m. p. 97°, which like the corresponding additive compound from phenylcarbimide and phenylmethylpyrazolone, namely, 1-*phenyl*-3-*methyl*-5-*pyrazolyl carbanilate*, colourless needles, m. p. 92—93°, is unstable, and when heated gives an odour of phenylcarbimide.

Ethyl phenylmethylpyrazoloneglyoxylate gives a *phenylhydrazone*, almost colourless needles, m. p. 182—183°, in the formation of which a difficultly isolable *isomeride*, yellow leaflets, is also produced; p-*bromophenylhydrazone*, yellowish-white needles, m. p. 213—214°.

1-*Phenyl*-3-*methyl*-5-*pyrazolone*-4-*glyoxylic acid*, yellowish-white needles, m. p. 236—238°, is obtainable by hydrolysis of the ester. With sulphuric acid it gives on warming a green coloration changing successively to red and brown, and at 200° it is converted with loss of carbon dioxide into the already known phenylmethylpyrazolonesulphonic acid (Möllenhoff, A., 1892, 1245). Heated with aniline at 150°, the acid gives rise to the *anil* of 1-*phenyl*-3-*methyl*-5-*pyrazolone*-4-*aldehyde*, greenish-yellow needles, m. p. 151—152°. The acid reacts slowly with phenylhydrazine in alcoholic solution at the ordinary temperature, giving rise to a *phenylhydrazone*, almost colourless needles, m. p. 205—206°, which can be esterified by alcohol and hydrogen chloride to the previously mentioned phenylhydrazone of the ester. If phenylmethylpyrazoloneglyoxylic acid is heated with methyl or ethyl alcohol for an hour in a sealed tube at 160—180°, orange-yellow needles of 1-phenyl-3-methyl-4-methylene-5-pyrazolone,

$$\begin{matrix}NPh-CO \\ | \\ N{=}CMe\end{matrix}\!\!>C{:}CH_2,$$

separate (compare Pellizzari, A., 1889, 517), a small amount of a colourless *substance*, m. p. above 280°, which in alcoholic solution gives a violet precipitate with ferric chloride being present in the mother liquor.

1 : 3-Diphenyl-5-pyrazolone condenses with ethyl oxalate under the same conditions as the above methylpyrazolone, giving the *sodium* or *potassium* derivatives of *ethyl* 1 : 3-*diphenyl*-5-*pyrazolone*-4-*glyoxylate*, which after acidifying is obtainable in yellowish-white, prismatic needles, m. p. 108—109°. The ester, which gives similar colour reactions to the analogous 1-phenyl-3-methyl compound, is, however, not hydrolysed on boiling with alcoholic potassium hydroxide; it gives a deep green *copper* derivative, m. p. 245—246° (decomp.); the *phenylhydrazone* as first obtained from reaction in chloroform or alcohol forms colourless needles, m. p. 208—209°, but on recrystallisation from alcohol passes into yellow, prismatic needles of an isomeride, m. p. 204—205°, which is directly produced in benzene solution.

1-*p*-Tolyl-3-methylpyrazolone, prepared from *p*-tolylhydrazine and ethyl acetoacetate, undergoes condensation with ethyl oxalate under the previous conditions, yielding yellow needles of the *potassium* derivative of *ethyl* 1-p-*tolyl*-3-*methyl*-5-*pyrazolone*-4-*glyoxylate*; this ester, which forms yellow needles, m. p. 87—88°, gives a deep red coloration with alcoholic ferric chloride, and a red changing to violet with common benzene and sulphuric acid.

1-p-*Tolyl-3-methyl-5-pyrazolone-4-glyoxylic acid* forms colourless needles, m. p. 218—219°. Treatment of the ester with the calculated quantity of phenylhydrazine gives a mixture of almost colourless needles and yellow leaflets. The former, purified by recrystallisation from alcohol, have m. p. 195—196°, whilst the latter, m. p. 209—210°, are obtained pure by crystallisation from warm chloroform; these two *phenylhydrazones* are isomeric, the structures:

$$\begin{matrix}NPh\cdot CO\\ N{=\!=}CMe\end{matrix}\!\!>CH\cdot C(:N\cdot NHPh)\cdot CO_2Et \quad \text{and}$$

$$\begin{matrix}NPh\cdot CO\\ N{=\!=}CMe\end{matrix}\!\!>C:C(\cdot NH\cdot NHPh)\cdot CO_2Et$$

being suggested for the colourless and yellow forms respectively. A similar explanation is proposed for the occurrence of the other isomeric phenylhydrazones described above.

Tolylmethylpyrazoloneglyoxylic acid with phenylhydrazine in benzene solution first gives colourless needles, m. p. 201—202°, of a *phenylhydrazine* salt, which loses a molecule of water on recrystallisation from hot alcohol, producing the *phenylhydrazone*, yellow leaflets, m. p. 217°. No isomerism was observed with this phenylhydrazone or with the *diphenylhydrazone* of ethyl tolylmethylpyrazoloneglyoxylate, prisms, m. p. 137—138°.

D. F. T.

Preparation of *N*-Halogenalkyl-5 : 5-dialkylbarbituric Acids. E. MERCK (D.R.-P. 265726).—*N*-Halogenalkyl-5 : 5-dialkylbarbituric acids of general formula $CRR_1\!<\!\begin{matrix}CO\cdot NX\\ CO\cdot NY\end{matrix}\!>\!CO$ (where R and R_1 are alkyl, X halogenalkyl, and Y hydrogen or halogenalkyl groups) are obtained when *N*-alkylen-5 : 5-dialkylbarbituric acids are treated with the required halogen, or when dialkylmalonyl haloids are combined with halogenated alkylcarbamides.

5 : 5-*Diethyl-1-allylbarbituric acid* forms colourless needles, m. p. 77°; and when treated (in cooled acetic acid solution) with bromine, gives rise to 5 : 5-*diethyl-1-βγ-dibromopropylbarbituric acid*,

$$CO\!<\!\begin{matrix}CEt_2\cdot CO\\ NH-CO\end{matrix}\!>\!N\cdot CH_2\cdot CHBr\cdot CH_2Br,$$

colourless needles, m. p. 126° (corr.); the latter compound can also be prepared by heating βγ-dibromopropylcarbamide,

$$CH_2Br\cdot CHBr\cdot CH_2\cdot NH\cdot CO\cdot NH_2,$$

with diethylmalonyl chloride during fifteen to twenty hours at 120°.

5 : 5-*Dibenzyl-1 : γ-bromopropylbarbituric acid*, small, hard prisms, m. p. 111°, is obtained in a similar manner from 5 : 5-dibenzyl-1-allylbarbituric acid.

5 : 5-*Diethyl-1-βγ-dichloropropylbarbituric acid* has m. p. 127°, and 5 : 5-*diethyl-1 : γ-bromopropylbarbituric acid*, m. p. 100°.

When 5-*phenyl-5-ethyl-1-allylbarbituric acid*, m. p. 68—69° (prepared from allylcarbamide and phenylethylmalonyl ester) is treated with bromine it gives rise to 5-*phenyl-5-ethyl-1-βγ-dibromopropylbarbituric acid*, $C_{15}H_{16}O_3N_2Br_2$, whilst 5 : 5-*diethyl-βγβ′γ′-tetrabromo-1 : 1-dipropylbarbituric acid*, $C_{14}H_{20}O_3N_2Br_4$, colourless prisms, m. p. 64°, is obtained by brominating 5 : 5-diethyl-1 : 1-diallylbarbituric acid

or by brominating *s*-diallylcarbamide and heating the *tetrabromodipropylcarbamide* with diethylmalonyl chloride at 120—130° for twenty-five hours in a vacuum. F. M. G. M.

Products of Decomposition of Indigo in the Vat. HERBERT EHRHARDT (*J. Soc. Dyers*, 1913, **29**, 321—322).—The loss of dye which is often experienced when indigo vats are reduced, not by pure solutions of sodium hyposulphite, but by metallic reducing agents, is traced to the formation of anthranilic acid. A vat containing 200 grams of pure 20% indigo-paste, 120 grams of lime slaked with 600 c.c. of water, 200 c.c. of sodium hydrogen sulphite solution of 57° Tw., and 30 grams of zinc was left for a few days. The sediment was then filtered and extracted with boiling water, whilst the solution was oxidised by a current of air and the precipitated indigo extracted with dilute hydrochloric acid. The combined solutions were then cooled, roughly titrated with sodium nitrite, and treated with the requisite amount of β-naphthol, when 2 grams of the azo-dye of anthranilic acid were obtained. J. C. W.

Formation of Pyrazine Compounds from Quinoxaline Derivatives. K. A. BÖTTCHER (*Ber.*, 1913, **46**, 3084—3087. Compare Gabriel and Sonn, A., 1908, i, 60).—2-*Methylquinoxaline*,

$$C_6H_4{<}\begin{matrix}N{:}CMe\\ |\\ N{:}CH\end{matrix},$$

b. p. 245—247°, is formed by the condensation of *o*-phenylenediamine with oximinoacetone in aqueous acetic acid solution. It solidifies in a freezing mixture of ice and salt, and is rapidly discoloured on exposure to sunlight. The *platinichloride*, unstable, yellow needles, darkens at 130°, and is not melted at 250°, whilst the *gold* salt softens at 122° and has m. p. 135° (decomp.). The *picrate* blackens below 200° and has m. p. 215°. Oxidation with alkaline permanganate converts 2-methylquinoxaline into 2-*methylpyrazine*-5 : 6-*dicarboxylic acid*,

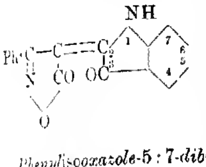
$$\begin{matrix}CMe\cdot N{:}C\cdot CO_2H\\ \|\qquad\quad |\\ CH-N{:}C\cdot CO_2H\end{matrix},$$

which, after purification through the *calcium* and *barium* salts, has m. p. 196°. The *copper* salt, $C_7H_4O_4N_2Cu,H_2O$, pale blue needles which decompose below the m. p., and the *silver* salt, $C_7H_4O_4N_2Ag_2$, were analysed.

2 : 3-Dimethylquinoxaline (compare Gabriel and Sonn, *loc. cit.*) crystallises with $2H_2O$. 2 : 3-Dimethylpyrazine-5 : 6-dicarboxylic acid, after purification by means of the barium salt, has m. p. 190°, instead of 200° as previously recorded. When treated with methyl alcohol and hydrogen chloride, it yields an oily *methyl* ester, which is also prepared by the action of methyl iodide on the silver salt. The *diamide*, needles, m. p. 227°, is obtained by the action of methyl alcoholic ammonia on the ester. H. W.

Indigoid Derivatives of Phenyl*iso*oxazolone. ANDRÉ MEYER (*Bull. Soc. chim.*, 1913, [iv], **13**, 992—1000).—The author has prepared a number of indigoid derivatives from phenyl*iso*oxazolone or its substituted derivatives as follows. Phenyl*iso*oxazole-2-indole,

prepared by heating indoxylic acid with dibromophenyl*iso*oxazolone in acetic acid in the presence of sodium acetate, crystallises from glacial acetic acid in red needles (compare Wahl, A., 1909, i, 261). In order to study the effect of substitution on the colour and properties of this indigoid dye, the author has prepared the following derivatives by the condensation of substituted isatin chlorides with phenyl*iso*oxazolone, which gives substances with the general constitution (annexed formula).



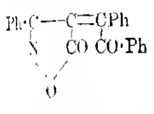
*Phenyl*iso*oxazole-5-bromo-2-indole* crystallises from acetic acid in deep, reddish-brown needles, its properties being closely allied to those of the non-halogenated indigoid dye.

*Phenyl*iso*oxazole-5 : 7-dibromo-2-indole* crystallises in red plates, its colour being brighter and its solubility in organic solvents much greater than that of the two preceding compounds.

*Phenyl*iso*oxazole-2-nitroindole*, scarlet-red needles, m. p. 220°, gives an eosin-red solution in concentrated sulphuric acid.

β-Naphthisatin chloride reacts similarly with phenyl*iso*oxazolone, giving *phenyl*iso*oxazole-2-β-naphthindole*, crystallising from ethylene bromide in brown needles.

Oxythionaphthen reacts with dibromophenyl*iso*oxazolone in acetic acid solution, yielding *phenyl*iso*oxazole-2-thionaphthen*, crystallising in scarlet red needles, giving a greenish coloration with sulphuric acid and a deep red precipitate from benzene solution with stannic chloride.



Phenyl*iso*oxazolone, unlike other heterocyclic compounds, such as indoxyl and oxythionaphthen, does not condense with cyclic ketones to give any well-defined products, but with benzil in alcoholic solution in the presence of piperidine the author has succeeded in preparing *phenyl*iso*oxazoledibenzil* (annexed formula), yellow needles, m. p. 208°.

W. G.

3 : 6-Diaminoacridine. Relationships between Acridine Derivatives and Analogous Phenazine Compounds. EUGÈNE GRANDMOUGIN and K. SMIROUS (*Ber.*, 1913, 46, 3425—3434).—In view of the similarity in the structure of 3 : 6-diaminoacridine (Benda, A., 1912, i, 651) and 3 : 6-diaminophenazine, the authors have undertaken a comparison of the behaviour of these two compounds and their derivatives, the present paper dealing particularly with the salt-formation and diazotisation of the first-mentioned compound. The salts of 3 : 6-diaminoacridine with one equivalent of acid are quite stable, whilst those with two or three equivalents are readily hydrolysed by water.

Addition of alkali to a concentrated solution of 3 : 6-diamino-10-methylacridinium chloride (trypaflavine of Ehrlich and Benda this vol., i. 904) precipitates the orange-yellow *imine base*,

$$NH_2\cdot C_6H_3<{}^{-CH-}_{NMe}>C_6H_3:NH,$$

ethereal solutions of which, when shaken with water, yield the *ammonium base*, $NH_2\cdot C_6H_3<{CH \atop NMe(OH)}>C_6H_3\cdot NH_2$, the latter being converted by heating with water into the *carbinol base*,

$$NH_2\cdot C_6H_3<{CH(OH) \atop NMe}>C_6H_3\cdot NH_2.$$

On diazotisation, 3 : 6-diaminoacridine yields a violet monodiazo-compound, which on account of its colour is considered to have a *p*-quinonoid structure: $NH{:}C_6H_3<{CH \atop NH}>C_6H_3\cdot N_2Cl$.

The diazo-compound combines with resorcinol, β-naphthol, and R-salt to form reddish-brown to reddish-violet *azo-dyes*, and is reduced by alcohol to 3-*aminoacridine*, m. p. 170°, which is orange-yellow in colour, yields yellow aqueous solution having a green fluorescence, and can be further diazotised and reduced to acridine.

On treatment with potassium iodide, the monodiazo-compound yields 3-*iodo*-6-*aminoacridine*, orange crystals, m. p. 230° (decomp.).

Diazotisation with excess of sodium nitrite in concentrated sulphuric acid solution yields a bisdiazo-compound, which, with potassium iodide, gives rise to 3 : 6-*di-iodoacridine*. This forms dark brown crystals of a metallic lustre, m. p. 270° (decomp.), and, when methylated by means of methyl sulphate in nitrobenzene solution and subsequently treated with potassium iodide, is converted into an orange-yellow, crystalline 3 : 6-*di-iodo*-10-*methylacridinium iodide*.

The *dihydrochloride* of 3 : 6-diaminoacridine, prepared by the addition of concentrated hydrochloric acid to an alcoholic solution of the monohydrochloride, crystallises in orange-yellow needles.

The *trihydrobromide*, obtained from the free base and alcoholic hydrogen bromide, forms orange crystals. The *monohydrochloride* of 3 : 6-diacetylaminoacridine forms slender, yellow crystals.

3 : 6-*Diamino*-10-*methylacridinium dihydrochloride*, prepared by the action of methyl sulphate on 3 : 6-diacetylaminoacridine in nitrobenzene solution, and subsequent hydrolysis of the resulting brownish-yellow *methosulphate* by means of hydrochloric acid, forms dark brownish-red crystals of a metallic lustre, and when warmed readily loses hydrogen chloride with the formation of the monohydrochloride.

3 : 6-*Diamino*-10-*methylacridinium bromide* forms Bordeaux-red leaflets of a metallic lustre, the *iodide*, orange needles, and the *nitrate*, reddish-brown needles.

The diazotisation of safranine has also been studied. According to Kehrmann, Havas, and Grandmougin (this vol., i, 1241), the green safranine salts formed by the combination of one molecule of the base with three equivalents of acid, consist of a mixture of the yellow *o*-quinonoid salt I and the blue *p*-quinonoid salt II:

$$\text{(I.)}\quad NH_3X\cdot C_6H_3 \lessgtr {N \atop NPhX} > C_6H_3\cdot NH_3X$$

$$\text{(II.)}\quad NH_3X\cdot C_6H_3<{N \atop NPhX}>C_6H_3{:}NH,HX.$$

Of these two salts only the *o*-quinonoid form should be capable of complete diazotisation.

This view has been confirmed by the behaviour of phenosafranine, which on treatment with solid sodium nitrite in concentrated sulphuric acid solution is partly converted into a bisdiazo-compound. If the solution is kept, the *p*-quinonoid salt II is slowly transformed into the *o*-quinonoid form and then undergoes complete diazotisation.

Reduction of the resulting solution by means of alcohol yields the phenylphenazonium of Kehrmann (A., 1897, i, 107). F. B.

The Degradation of Allantoin to Hydroxonic Acid, and a New Synthesis of Allantoin. HEINRICH BILTZ and ERHARD GIESLER (*Ber.*, 1913, **46**, 3410—3425).—Allantoin, prepared from uric acid by oxidation with alkaline potassium permanganate solution, was further oxidised to potassium allantoxanate; by treating this in aqueous solution with slightly less than the calculated amount of *N*-sulphuric acid, more than 90% of the theoretical quantity of allantoxaidin (from decomposition of the unisolable allantoxanic acid,

$$\begin{matrix} CO\cdot NH \\ | \\ NH-CO \end{matrix}\!\!>C{:}N\cdot CO_2H),$$

was obtainable (compare Ponomarev, A., 1879, 226, 228, 461); the allantoxaidin, $CO<\begin{matrix} NH\cdot C{:}NH \\ | \\ NH\cdot CO \end{matrix}$, was obtained in short prisms containing $1H_2O$, and of m. p. 282° (decomp.); its aqueous solution on heating yields biuret and formic acid, and a similar decomposition ensues on heating the substance with acetic anhydride, the product being *formylacetylbiuret*, probably $CHO\cdot NH\cdot CO\cdot NH\cdot CO\cdot NHAc$, leaflets, m. p. 184—185°.

The reduction of potassium allantoxanate by sodium amalgam and water (compare Ponomarev, *loc. cit.*) gave rise to the product described by Ponomarev as hydroxonic acid, $C_8H_{10}O_7N_6$, but when this was purified by means of the ester, it was found to be of the composition $C_4H_5O_4N_3$, that is, *dihydroallantoxanic acid*,

$$\begin{matrix} CO\cdot NH \\ | \\ NH-CO \end{matrix}\!\!>CH\cdot NH\cdot CO_2H;$$

potassium salt, rectangular prisms, rapid decomp. near 333°; *ammonium* salt, colourless needles, unfused even at 340; *silver* salt with $1H_2O$; *methyl* ester, leaflets, m. p. 275° (decomp.); *ethyl* ester, rectangular tablets, m. p. 277° (decomp.).

The above results indicate that allantoin is the amide of dihydroallantoxanic acid, but it was not found possible to convert the esters of the latter substance into allantoin, nor was it possible to obtain allantoxanic acid directly from allantoin, but the existence of the relationship could be demonstrated in the following manner.

When hydroxonic acid is boiled with acetic anhydride for eight hours, it undergoes loss of carbon dioxide with formation of 1:3:6-*triacetyl-5-aminohydantoin*, $\begin{matrix} CO\cdot NAc \\ | \\ NAc-CO \end{matrix}\!\!>CH\cdot NHAc$, tablets from acetone or prisms from benzene, m. p. 184—185°; this substance when boiled with alcohol gives leaflets, m. p. 240—241°, of 1:6-*diacetyl-5-aminohydantoin*, which on evaporation with concentrated hydrochloric acid is converted into *5-aminohydantoin hydrochloride*, m. p. 218—222°

(decomp.); the free base, of which the *platinichloride* was also prepared, could not be isolated; the action of silver oxide on the hydrochloride produced insoluble 3-*silver*-5-*aminohydantoin*. Allantoin itself was obtainable from the hydrochloride of the aminohydantoin by treatment with potassium cyanate in aqueous solution. D. F. T.

Ring Formation between the Nitro- and Amino-groups with Production of Triazines. Fritz Arndt (*Ber.*, 1913, 46, 3522—3530).—The preparation and properties of a number of triazines are described which are obtained from *o-nitrophenylguanidine* and *o*-nitrophenylcarbamide by loss of water under the influence of sodium or potassium hydroxide. Since neither sodium carbonate, ammonia nor acids bring about this change, it seems probable that ring formation is preceded by formation of the alkali salt of the ψ-nitro-form. This is the more likely, since the originally orange-yellow solution becomes red when warmed with alkali, and then yields a yellow precipitate. After ring formation, the reverse change immediately occurs, since the product obtained does not possess the properties of an *o*-quinone.

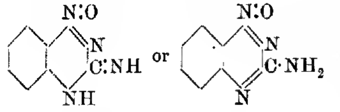
If Angeli's formula for the azoxy-group (this vol., i, 658) is adopted, the compounds obtained by the author may be regarded as containing this group in the triazine ring, and it therefore seems to be produced with remarkable ease by loss of water from an amino- and nitro-group, when ring formation can simultaneously occur.

o-Nitrophenylguanidine nitrate, pale yellow prisms, m. p. 160°, is obtained by the addition of 2*N*-nitric acid to the product of the action of concentrated hydrochloric acid on a mixture of *o*-nitroaniline and cyanamide. Should the latter contain dicyanamide, the white, amorphous *nitrate* of a condensation product of cyanamide and dicyanamide is also formed. *o*-Nitrophenylguanidine,

$$NO_2 \cdot C_6H_4 \cdot NH \cdot C(:NH) \cdot NH_2,$$

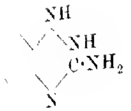
separates as a viscous oil when the finely powdered nitrate is treated with cold 2*N*-sodium hydroxide. It separates from its aqueous solution in orange-yellow needles which contain $1H_2O$, m. p. 53°.

Aminophenotriazoxine [3-*amino*-1 : 2 : 4-*benzotriazine* 1-*oxide*] (annexed formula), shining leaflets, m. p. 269°, is obtained in almost quantitative yield by the action of boiling sodium hydroxide solution on *o*-nitrophenylguanidine or on the crude reaction mixture obtained from *o*-nitroaniline, cyanamide and hydrochloric acid. The *hydrochloride*, *sulphate*, and *nitrate* were examined. The *silver* salt, $C_7H_5ON_4Ag$, was analysed.



Sodium nitrite and hydrochloric acid convert 3-amino-1 : 2 : 4-benzotriazine oxide directly into 3-*hydroxy*-1 : 2 : 4-*benzotriazine* 1-*oxide*, yellow leaflets, m. p. 219° (decomp.).

Aminobenzotriazine oxide is readily reduced by tin and hydrochloric acid; when 2*N*-nitric acid is added to the reaction product, 3-*amino*-



dihydro-1:2:4-*benzotriazine nitrate*, m. p. 195—197° (decomp.), is obtained. When an aqueous solution of this salt is treated with sodium carbonate, the free *base* (annexed formula) separates in white leaflets which rapidly become oxidised with formation of 3-*amino*-1:2:4-*benzotriazine*, yellow needles, m. p. 207°. The latter substance is best obtained by the action of potassium ferricyanide and sodium hydroxide on a solution of dihydroaminophentriazine nitrate.

For the preparation of *o-nitrophenylcyanamide*, $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}CN$, an intimate mixture of *o*-nitroaniline hydrochloride and lead thiocyanate is allowed to remain at the ordinary temperature until a portion does not melt when placed in boiling water; the mixture is then heated for six to seven hours on the water-bath, and subsequently boiled with 2*N*-sodium hydroxide; after removal of lead sulphide, the solution is cooled, filtered from unchanged *o*-nitroaniline, and cautiously acidified with hydrochloric acid, when *o*-nitrophenylcyanamide, pale yellow needles, m. p. 152°, separates in poor yield. Boiling dilute hydrochloric acid transforms it into *o*-nitrophenylcarbamide, yellow needles, m. p. 183—184° (Schwartz [A., 1897, i, 411] gives 181°), which is converted by boiling potassium hydroxide into hydroxybenzotriazine oxide, identical with the product obtained from aminobenzotriazine oxide.

Attempts to prepare *o*-nitrophenylthiocarbamide were unsuccessful.

H. W.

A Mode of Decomposition of Halogenated Alkyl Derivatives of Hexamethylenetetramine. MARCEL SOMMELET (*Compt. rend.*, 1913, **157**, 852—854. Compare Hock, A., 1903, i, 465).—Derivatives of hexamethylenetetramine of the type $C_6H_{12}N_4RX$, where R is an alkyl group and X one of the halogens, are decomposed by boiling with water. This is particularly true of the derivative obtained from benzyl chloride, the products of the decomposition being benzaldehyde (70—80% yield) and a mixture of bases of which the following were characterised: ammonia, methylamine, dimethylamine, trimethylamine, and benzylamine. Benzaldehyde is similarly obtained by boiling benzyl chloride and hexamethylenetetramine together in aqueous alcoholic solution.

The three xylyl bromides combine directly with hexamethylenetetramine in chloroform solution to give the additive *compounds*, $C_6H_{12}N_4Br{\cdot}CH_2{\cdot}C_6H_4Me$, having melting points respectively, *ortho*, 198°; *meta*, 215°; *para*, 216°. Each of these are similarly decomposed by boiling with water, giving the corresponding tolualdehydes.

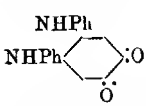
The course of this decomposition reaction is not yet clear, but the relatively abundant production of methylamine points to the possible primary production of benzylmethyleneamine, which undergoes isomerisation to benzylidenemethylamine:

$$CH_2Ph{\cdot}N{:}CH_2 \longrightarrow CHPh{:}NMe.$$

W. G.

Anilinoquinones and their Azine Derivatives. FRIEDRICH KEHRMANN and MARCELIEN CORDONE (*Ber.*, 1913, **46**, 3009—3014).—The authors have convinced themselves of the correctness of Willstätter's view as to the holoquinonoid nature of both modifications of *o*-benzoquinone, but believe that these merely represent dimorphous forms of the same substance. *o*-Benzoquinone is said to present an example of dichroism, on account of which the different crystalline forms appear to be of different colours; the less stable form is stated to be not colourless but green. Both forms of the substance are, therefore, of diketonic structure.

If catechol is oxidised in the presence of aniline by silver acetate in solution in cold acetic acid, a brown mixture of 4 : 5-*dianilino*-o-*benzoquinone* (annexed formula), brownish-red needles, m. p. 193°, with a little of the trianilino-compound separates; the former is easily extracted by sodium hydroxide, in which it is soluble.



When equimolecular quantities of the above dianilinobenzoquinone and *o*-phenylenediamine hydrochloride are heated together in concentrated solution in alcohol, condensation occurs to 2 : 3-*dianilinophenazine*,

$$C_6H_2(NHPh)_2 \lessgtr {}^{N}_{N} > C_6H_4,$$

orange-yellow, apparently rhombohedral crystals, m. p. 218—219°, which separate from alcohol with one C_2H_6O; the *hydrochloride*, which is the primary product, forms long, deep red needles.

A similar condensation could be effected between the dianilino-o-benzoquinone and phenyl-*o*-phenylenediamine hydrochloride, the product being 2 : 3-dianilino-10-phenylphenazonium chloride,

$$C_6H_2(NHPh)_2 \lessgtr {}^{N}_{NPhCl} > C_6H_4,$$

violet tablets, m. p. 235—237° (compare Fischer and Hepp, A., 1896, i, 50).

Under similar conditions to the above, 3-anilino-4-hydroxy-*o*-benzoquinone (Zincke, A., 1885, 787) condenses with *o*-phenylenediamine hydrochloride; producing long, deep red needles of the *hydrochloride* of 2-*anilino*-3-*hydroxyphenazine*; the free base forms brownish-red needles, decomp. above 200°. Condensation with phenyl-*o*-diphenylenediamine gave rise to two products which are probably 3-anilino-2-hydroxy-10-phenylphenazonium chloride and 2-anilino*apo*safranone,

$$C_6H_4 < {}^{N}_{NPh} \gg C_6H_2(NHPh)O,$$

The constitution of the above dianilino-*o*-benzoquinone is demonstrated by hydrolysis with dilute solutions of alkali, which gives rise to the *s*-dihydroxyquinone of Nietzki and Schmidt (A., 1888, 1181). Of the three possible isomerides having the composition of a dianilinoquinone, two are already known, so that to this third isomeride is to be ascribed the remaining structure, 4 : 5-dianilino-*o*-benzoquinone.

D. F. T.

Purines. XII. CARL O. JOHNS and EMIL J. BAUMANN (*J. Biol. Chem.*, 1913, **15**, 515—521. Compare this vol., i, 774, 1000).—5-Amino-6-ethylamino-2-hydroxy-4-methylpyrimidine reacts smoothly with the reagents commonly used for the preparation of purines. Thus, when the formyl derivative is heated, *2-oxy-6-methyl-9-ethylpurine*, $\begin{matrix}\mathrm{N{:}CMe{\cdot}C{-\!\!-}N} \\ \mathrm{CO{\cdot}NH{\cdot}C{\cdot}NEt}\end{matrix}\!\!>\!\mathrm{CH}$, is formed. This crystallises in a net work of silky needles, which begin to melt at 256°, m. p. 275° (decomp.).

Similarly, the corresponding acetyl derivative yields *2-oxy-6 : 8-dimethyl-9-ethylpurine*, which also forms a network of silky needles, m. p. 265° (decomp.) to a dark oil.

2-Oxy-8-thio-6-methyl-9-ethylpurine is formed when the diaminopyrimidine is heated with thiocarbamide; it crystallises in colourless sheaves, decomp. 295—300°. When the components are mixed in hot water, a thiocarbamide additive product of the pyrimidine is obtained; this has m. p. 204—206° (decomp.), and gives the thiopurine when heated.

The thiopurine reacts with monochloroacetic acid, forming *2-oxy-6-methyl-9-ethylpurine-8-thiolacetic acid*,

$$\begin{matrix}\mathrm{N{:}CMe{\cdot}C{-\!\!-}N} \\ \mathrm{CO{\cdot}NH{\cdot}C{\cdot}NEt}\end{matrix}\!\!>\!\mathrm{CS{\cdot}CH_2{\cdot}CO_2H}.$$

This separates as a bulky mass of needles, which darken at 270°. It is stable in hot water, but boiling with concentrated hydrochloric acid hydrolyses it to 2 : 8-dioxy-6-methyl-9-ethylpurine.

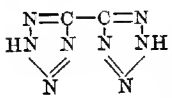
The action of thiophosphoryl chloride on 4 : 5-diamino-6-hydroxy-2-methylthiolpyrimidine converts it into *6-oxy-8-thio-2-methylthiolpurine*, $\begin{matrix}\mathrm{NH{\cdot}CO{\cdot}C{\cdot}NH} \\ \mathrm{SMe{\cdot}C{-\!\!-}N{-\!\!-}C{\cdot}NH}\end{matrix}\!\!>\!\mathrm{CS}$. This separates in small globules, which begin to decompose at 275°, and give the murexide test. E. F. A.

Purines. XIII. **2 : 8-Dioxy-1 : 6-dimethyl-1 : 2 : 8 : 9-tetrahydropurine and 5-Nitro-3 : 4-dimethyl-1 : 2 : 3 : 6-tetrahydropyrimid-2 : 6 dione (α-Nitrodimethyluracil).** CARL O. JOHNS and EMIL J. BAUMANN (*J. Biol. Chem.*, 1913, **16**, 135—142).—Methyl sulphate and an aqueous solution of the sodium salt of 5-nitro-6-amino-4-methyl-2 : 3-dihydro-2-pyrimidone react at the ordinary temperature to form, in 80% yield, *5-nitro-6-amino-3 : 4-dimethyl-2 : 3-dihydro-2-pyrimidone*, $\mathrm{CO}\!<\!\begin{matrix}\mathrm{N{:}C(NH_2)} \\ \mathrm{NMe{\cdot}CMe}\end{matrix}\!>\!\mathrm{C{\cdot}NO_2}$, decomp. 170—195°, prisms containing $\frac{1}{2}H_2O$. The position of the new methyl group is established as follows. By heating with 25% sulphuric acid at 160°, the substance is converted into *5-nitro-3 : 4-dimethyl-1 : 2 : 3 : 6-tetrahydropyrimid-2 : 6-dione*, $\mathrm{CO}\!<\!\begin{matrix}\mathrm{NH{-\!\!-}CO} \\ \mathrm{NMe{\cdot}CMe}\end{matrix}\!>\!\mathrm{C{\cdot}NO_2}$, m. p. 191°, slender prisms (the only other possible 5-nitrodimethyl-1 : 2 : 3 : 6-tetrahydropyrimid-2 : 6-dione is Lehmann's 5-nitro-1 : 4-dimethyl-1 : 2 : 3 : 6-tetrahydropyrimid-2 : 6-dione, m. p. 149°), which is oxidised by nitric acid, D 1·5, and concentrated sulphuric acid on the water-bath to 5-nitro-3-methyl-1 : 2 : 3 : 6-tetrahydropyrimid-2 : 6-dione-4-carboxylic acid, which cannot be

isolated, since it loses carbon dioxide and changes to Behrend's 5-nitro-3-methyl-1 : 2 : 3 : 6-tetrahydropyrimid-2 : 6-dione, m. p. 255°.

The reduction of 5-nitro-6-amino-3 : 4-dimethyl-2 : 3-dihydro-2-pyrimidone by aqueous ammonia and ferrous sulphate produces 5 : 6-*di-amino-3 : 4-dimethyl-2 : 3-dihydro-2-pyrimidone*, $C_6H_{10}ON_4$, decomp. about 230°, colourless plates, in 40% yield; the latter and an equal weight of carbamide at 170—180° produce 2 : 8-*dioxy*-1 : 6-*dimethyl*-1 : 2 : 8 : 9-*tetrahydropurine*, $\begin{matrix}NMe\cdot CMe\colon C\cdot NH\\ | \qquad\qquad\quad |\\ CO—N\!\!=\!\!C\cdot NH\end{matrix}\!\!>\!CO$, decomp. 260—265°, prisms containing H_2O; by evaporating the latter with nitric acid and treating the yellow residue with an alkali, a rose coloration is developed. C. S.

Bistetrazole and Isomeric Derivatives of Tetrazole. E. OLIVERI-MANDALÀ and T. PASSALACQUA (*Gazzetta*, 1913, 43, ii, 465—474. Compare A., 1912, i, 144).—When cyanotetrazole (*loc. cit.*) is further acted on with azoimide, or when cyanogen is passed into an aqueous solution of azoimide as in the experiment formerly described, but using a more concentrated solution, bistetrazole and the amide of tetrazolecarboxylic acid are produced in addition to cyanotetrazole, which still forms the chief product of the reaction. Saponification of the cyanotetrazole yields (by way of the unstable carboxylic acid) tetrazole, and this is the best way of preparing this substance. The preparation is conveniently carried out by heating the sodium salt described below with hydrochloric acid, evaporating to dryness, and extracting the tetrazole with warm acetone.



Bistetrazole (annexed formula) forms prismatic crystals, m. p. 254—255° (decomp.). Bistetrazole and especially its *silver* salt are explosive. The substance has about the calculated molecular weight in freezing water. The *barium* salt, $C_2N_8Ba,3H_2O$, was prepared. Bistetrazole is decomposed by warm, concentrated sulphuric acid according to equation: $C_2H_2N_8+2H_2O+O_2=3N_2+2CO_2+2NH_3$, so that the sulphuric acid acts as an oxidiser.

The above-mentioned *tetrazole-5-carboxylamide*, $C_2H_3ON_5$, has m. p. 234° (decomp.). *Sodium 2-sodiotetrazole-5-carboxylate*, $C_2O_2N_4Na_2$, is obtained by saponification of the amide or of the cyanotetrazole. The *barium* salt has the composition $C_2N_4O_2Ba,3\frac{1}{2}H_2O$.

5-*Cyano-2-methyltetrazole*, $C_3H_3N_5$, b. p. 100—102°/16 mm., is obtained by boiling the silver salt of 5-cyanotetrazole with an ethereal solution of methyl iodide. When it is saponified with alcoholic sodium hydroxide, the *sodium* salt of the corresponding acid, $C_3H_3O_2N_4Na$, is produced, and from this the free 2-*methyltetrazole-5-carboxylic acid*, $C_3H_4O_2N_4$ (prisms, m. p. 204—205°, losing CO_2), can be prepared. When this acid is heated at its m. p., 2-*methyltetrazole*, $C_2H_4N_4$, b. p. 145—147°/759 mm., is obtained.

When the silver salt of tetrazole and ethyl iodide are heated in benzene solution for some hours, 2-ethyltetrazole and 1-ethyltetrazole are produced. 2-*Ethyltetrazole*, $C_3H_6N_4$, has b. p. 70—71°/35 mm., or

152—155° at ordinary pressure. 1-*Ethyltetrazole*, $C_3H_6N_4$, has b. p. 162—164°/30 mm. R. V. S.

The Hydrolytic Constants of Some Derivatives of Tetrazole. E. OLIVERI-MANDALÀ (*Gazzetta*, 1913, **43**, ii, 487—493. Compare preceding abstract).—Measurements of the catalysis of methyl acetate give the following values for the constants of hydrolysis: 2-methyltetrazole, 0·00026; 1-methyltetrazole, 0·000047; 2-ethyltetrazole, 0·00049; 1-ethyltetrazole, 0·00014. R. V. S.

Action of Nitrogen Peroxide on Aliphatic Diazo-compounds and on Tetrazens. HEINRICH WIELAND and CURT REISENEGGER (*Annalen*, 1913, **401**, 244—251).—Ethyl diazoacetate and nitrogen peroxide react in cold benzene to form ethyl dinitroacetate and nitrogen, ethyl furoxandicarboxylate being obtained as a by-product. Similarly, at the ordinary temperature, nitrogen peroxide and diazodeoxybenzoin yield ωω-dinitrotoluene, probably by the decomposition of the initially formed benzoyl derivative.

Nitrogen peroxide and diphenyleneazomethylene (Staudinger and Kupfer, A., 1911, i, 751) react in cold benzene in the absence of moisture to form nitrogen and 9 : 9-*dinitrofluorene*, $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}>C(NO_2)_2$, m. p. 128° (decomp.), colourless needles, which yields fluorenone above its m. p.

Nitrogen peroxide and tetraphenyltetrazen in cold benzene yield a deep green solution of an additive compound, which decomposes at the ordinary temperature with the formation of pp′-*dinitrotetraphenyltetrazen*, $NO_2·C_6H_4·NPh·N:N·NPh·C_6H_4·NO_2$, decomp. 160°, orange-yellow crystals.

The substance is proved to be a tetrazen by the liberation of nitrogen and the production of an intensely blue solution by treatment with concentrated sulphuric acid; the positions of the nitro-groups are proved by reduction, whereby ammonia and *p*-aminodiphenylamine (2 mols.) are produced. In a similar reaction, nitrogen peroxide and diphenyldiethyltetrazen yield *di*-p-*nitrophenyldiethyltetrazen*, $C_{16}H_{18}O_4N_6$, orange-red needles, which is converted into *p*-phenylene-ethyldiamine by reduction. C. S.

The Real Nature of the So-called Artificial Globulin. HUBERT W. BYWATERS and D. G. C. TASKER (*J. Physiol.*, 1913, **47**, 149—158).—Several observers have stated that on keeping, the serum albumin in blood and urine is converted into globulin. The artificial product when analysed is found not to be identical with the natural globulin, but it is really alkaline meta-protein. W. D. H.

Colloidal Properties of Hæmoglobin. Modifications of the Viscosity and Surface Tension of Suspensions of Methæmoglobin by the Action of Hydrochloric Acid or Sodium Hydroxide. II. FILIPPO BOTTAZZI (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 263—270).—The viscosity and surface tension of aqueous suspensions of methæmoglobin (compare this vol., i, 1249), previously

purified by dialysis for four months or longer, differ little from those of distilled water. When the methæmoglobin is brought into solution by means of hydrochloric acid or sodium hydroxide, increased viscosity and diminished surface tension are shown by the liquid, which is at first a suspension solution and finally yields a perfect solution. Continued addition of acid or alkali does not lower the surface tension beyond a certain value, which seems to be independent of the concentration of the dissolved methæmoglobin so long as this lies within certain limits; neutralisation of the acid (alkali) with an equal volume of alkali (acid) causes precipitation of the methæmoglobin and increase of the surface tension.

The increased velocity caused by hydrochloric acid diminishes considerably when excess of acid is added, and tends to return to its original value, although no precipitation occurs. This seems to be due to the influence of the acid in lowering the dissociation of the methæmoglobin chloride, and hence the concentration of the methæmoglobin ions, on which the increased viscosity depends.

Addition of sodium chloride to solution of sodium methæmoglobinate produces a further small, constant diminution in the surface tension, although the salt has no appreciable effect on a solution of pure methæmoglobin (compare Bottazzi and d'Agostino, this vol., ii, 115).

T. H. P.

Action of Quinones on Wool and Other Protein Substances. LOUIS MEUNIER (*Zeitsch. angew. Chem.*, 1913, 26, 616).—The results described by Scharvin (this vol., i, 661) have already been published by Meunier and incorporated in certain patents (compare A., 1908, i, 586, and D.R.-P. 240512). J. C. W.

Products of Hydrolysis of Thynnine and Percine. ALBRECHT KOSSEL and F. EDLBACHER (*Zeitsch. physiol. Chem.*, 1913, 88, 186—189).—Thynnine yields an aminovaleric acid, proline, and tyrosine on hydrolysis. The same acids were obtained from percine. Acids of the C_5-series play the chief part in the constitution of the protamines, C_6-acids being only occasionally present. The latter play the more important part in the higher proteins. E. F. A.

The Stability of Invertase. CARL NEUBERG (*Biochem. Zeitsch.*, 1913, 56, 495—497).—The invertase was found to be still intact in an expressed yeast juice which had been allowed to autolyse for 470 days. S. B. S.

Amylases. VI. A Comparison of Amyloclastic and Saccharogenic Powers. HENRY C. SHERMAN and M. D. SCHLESINGER (*J. Amer. Chem. Soc.*, 1913, 35, 1784—1790).—In the investigation of the action of amylase on starch, the amount of reducing sugar produced is not always proportional to the amount of starch apparently digested.

The authors find that with specimens of pancreatic amylase the amount of starch apparently digested (amyloclastic power) is about twice the amount of maltose produced (saccharogenic power), whilst

with malt amylase the ratio of maltose formed to starch apparently digested is much higher; indeed, with some specimens of the latter, the amount of maltose exceeds the quantity of starch apparently digested. The application of the starch-iodine coloration is therefore evidently not well adapted for the measurement of the starch-digesting power of malt amylase. D. F. T.

Amylases VII. The Forms of Nitrogen in Amylase Preparations from the Pancreas and from Malt, as Shown by the Van Slyke Method. HENRY C. SHERMAN and A. O. GETTLER (*J. Amer. Chem. Soc.*, 1913, **35**, 1790—1794).—Analysis has been made of various specimens of pancreatic and malt amylase by the Van Slyke method, and the results as to the nature and relative quantity of the hydrolytic products indicate that the amylase preparations used were essentially protein substances. All the eight forms of nitrogen recognisable by the Van Slyke method were present, the proportions being within the range of variation shown by typical protein substances. D. F. T.

The Partial Purification of the Esterase from Pig's Liver. GEORGE PEIRCE (*J. Biol. Chem.*, 1913, **16**, 1—3).—Pig's liver was ground up, strained, and water added, incubated at 37° for one day, and, after remaining several weeks at room temperature, was filtered. This crude enzyme solution was dialysed and filtered; dialysis removed about 90% of the solids, and the solution lost about 20% of its activity. Ammonium sulphate was then added nearly to half saturation and the liquid filtered. The precipitate was inactive. The filtrate was then fully saturated with the same salt, and filtered; the filtrate was inactive. The precipitate was then dissolved in water and dialysed until free from sulphate. This represents the most highly purified solution obtained; it was very active; no attempt was made to obtain a solid from it. W. D. H.

The Compound Formed between Esterase and Sodium Fluoride. GEORGE PEIRCE (*J. Biol. Chem.*, 1913, **16**, 5—18).—The compound formed between esterase (from pig's liver) and sodium fluoride has little if any action on ethyl butyrate. The formation of this compound is reversible. When the concentration of the fluoride is varied from 0·009 to 0·27 mg. per litre, the inhibition increases from 20 to 88%. The inhibiting effect hardly varies at all with the concentration of the enzyme. The conclusion is drawn that one molecule of the inactive compound contains 1 molecule of enzyme and 1 molecule of sodium fluoride. W. D. H.

The Stability of Carboxylase. CARL NEUBERG (*Biochem. Zeitsch.*, 1913, **56**, 497—498).—In a maceration juice prepared from an old dried yeast obtained by Lebedev's method, the carboxylase was found to be active when the zymase was no longer existent. The former ferment appears, therefore, to be the more stable. S. B. S.

Mercury Naphthalene Derivatives. JOHANNES GADAMER [with R. BRIEGER and WERNER SCHULEMANN] (*Zeitsch. angew. Chem.*, 1913, **26**, 627—631).—A lecture delivered before the Verein deut. Chemiker

at Breslau. Some mercury compounds of substituted naphthalenes are discussed, and it is shown how their unusual behaviour and inconstant composition may be explained by considering the residual affinities of the atoms and groups involved.

When the sodium salt of 8-amino-1-naphthol-3:5-disulphonic acid (*K*-acid) is digested with mercuric acetate, a bright red mercuriated substance is obtained. From its method of formation and its colour, it might be expected that the mercury is attached to a carbon atom, but the fact that ammonium sulphide causes precipitation of mercuric sulphide suggests that the metal is linked with nitrogen. The colour was destroyed by the addition of alkali or sodium chloride, but was reproduced on acidifying with a mineral acid. The varying mercury-content of the product suggested that not a chemical, but rather an adsorption, compound was present, but the fact that salt or strong acetic acid decolorised solutions of the substance is not in harmony with this view.

The influence of various substituents in the naphthalene nucleus was studied, and the following conclusions are drawn: the presence of $-OH$ or $-NH_2$ in the β-position hinders the fixation of mercury, only one atom of which enters the ortho-position; the presence of $-OH$ or $-NH_2$ in tho α-position permits of the entry of two mercury atoms in the ortho- and para-positions, giving compounds which are stable towards ammonium sulphide, but tend to form unstable, coloured quinonoid compounds in the presence of reagents which reduce the acidity of their solutions; when attempts are made to introduce more mercury into naphthol derivatives, alkali is found to remove the excess of mercury as the hydrosol of the hydroxide, but the naphthylamines can loosely fix more mercury, giving substances which are turned deep red by alkalis and decomposed by ammonium sulphide; sulphonic acid groups render the mercury compounds moro unstable.

In *K*-acid, the various effects indicated above are cumulative. Theso effects are discussed on theoretical grounds, and it is explained why these naphthalene derivatives can form compounds with indefinite quantities of mercury, in which there is no distinction between true chemical combination and adsorption. J. C. W.

Physiological Chemistry

Water in Expired Air. WILLIAM OSBORNE (*Proc. physiol. Soc.*, 1913, xii; *J. Physiol.*, **47**).—Galeotti states that the expired air is not fully saturated with aqueous vapour, but only about three-quarters saturated. Loewy and Gerhartz point out that this is incorrect, for the temperature of expired air is not 37°, but between 32·5° and 33·5°. The present experiments confirm the latter view, and the correct theoretical figures were obtained if the

temperature is assumed to be 33·9°. The experiments were made on men in whom loss of water by the skin was prevented by a rubber suit. Such experiments are only safe in winter, as a dangerous fever may arise if the external air is too warm.

W. D. H.

Acidosis. ERNEST L. KENNAWAY, MARCUS S. PEMBREY, and EDWARD P. POULTON (*Proc. physiol. Soc.*, 1913, x—xi; *J. Physiol.*, **47**).—In healthy men the value of the alveolar carbon dioxide pressure may fall below the normal (40 mm.) if carbohydrate food is withheld; in diabetes it may be normal; the determining factor is the extent of acidosis. It falls suddenly one or two days before the onset of fatal coma; a value of 25 is grave; one of 20 means that coma is imminent. Estimation of the acetone substances is not such a good guide, and suggestions are put forward to explain variations in the ratio between these substances. Their equilibrium point is probably connected with the degree of acidosis, and the high proportion of β-hydroxybutyric acid in marked cases may be due to a washing out of acetone from the blood by the increased pulmonary ventilation.

W. D. H.

The Carbon Dioxide and Oxygen Content of the Blood after Clamping the Abdominal Aorta and Inferior Vena Cava Below the Diaphragm. JOHN R. MURLIN, LEO EDELMANN, and B. KRAMER (*J. Biol. Chem.*, 1913, **16**, 79—101).—The changes found are consistent with the mechanical explanation of the altered respiratory quotient after clamping the vessels. When the quotient rose, the carbon dioxide of the blood fell; when it remained stationary, the carbon dioxide did not change; when it fell, the carbon dioxide rose. Clamping off the blood from the abdominal organs therefore does not alter the character of the metabolism.

W. D. H.

The Dissociation of Carbon Dioxide from Human Blood. JOHANNE CHRISTIANSEN, CLAUDE G. DOUGLAS, and JOHN S. HALDANE (*Proc. physiol. Soc.*, 1913, ii; *J. Physiol.*, **47**).—The experiments here briefly referred to show that the effect of oxygen on the carbon dioxide-carrying power of the blood is even more important than the well-known effect of carbon dioxide on its oxygen-carrying functions.

W. D. H.

The Combination of Hydrogen Arsenide in the Blood. RICHARD MEISSNER (*Chem. Zentr.*, 1913, ii. 705—706; from *Zeitsch. expt. Path. Ther.*, 1913, **13**, 284—300).—The absorption capacity of the various constituents of blood for the gas was estimated by Reckleben and Lockemann's method. All solutions or suspensions were shaken for the same period with the same amount of the arsenic compound. The various lipoids in suspension or in ether and chloroform solution have practically no combining capacity in quantities in which they occur in the blood. Even the brain can combine with no more hydrogen arsenide than can physiological

saline in which it is suspended. Of the other constituents, hæmatin possesses a marked combining capacity, and blood containing carbon monoxide is less liable to hæmolysis by the arsenic compound than normal blood. The combining capacity of the iron-free hæmatoporphyrin is much smaller than that of hæmatin. It appears that the iron plays some part in the combination of the various iron compounds investigated; only sodium nitroprusside evinced any marked combining capacity, for it yielded with hydrogen arsenide a solid substance containing both iron and arsenic. The antagonistic action of various substances to hydrogen arsenide poisoning was also investigated. Cholesterol and iodipin were without effect. Various colloidal silver and mercury preparations were also tried, but, although they combine with the arsenic compound, they were too toxic to the kidneys for *intra vitam* use. Of the other substances investigated, only cadmium chloride exhibited a high combining capacity. The *in vitro* action of the hydrogen arsenide on blood gives a product with a spectrum similar to thiomethæmoglobin. S. B. S.

The Fermentative Properties of Blood. II. The Peptolytic Ferments of Normal Animals. Ludwig Pincussohn and Hellmuth Petow (*Biochem. Zeitsch.*, 1913, **56**, 319—329).—In continuation of the work of Pincussohn (this vol., i, 788), many examples are given to illustrate the fact that the sera of animals are capable of degrading the peptones prepared (by sulphuric acid method) from the proteins of their own organs, but not from the organs of other animals and foreign proteins. An exception was found in the case of guinea-pig serum, and attention is called to the fact that this serum is used generally for supplying the complement in various hæmolytic systems. Guinea-pig's serum also degrades silk peptone. The serum also degrades peptones prepared from the organ proteins of closely allied species. Thus the serum from the fox also degrades peptones prepared from the organs of dogs, and dog's serum degrades peptones derived from fox tissues, but not from those of any other animals. The method may therefore be applied for determining the relationship of various species. S. B. S.

Phosphatides of the Stromata of the Red Blood Corpuscles of Sheep and Man. M. Bürger and H. Beumer (*Biochem. Zeitsch.*, 1913, **56**, 446—456).—The stromata of sheep were precipitated by carbon dioxide from the lysed blood and dried. They yielded an ethereal extract, which consisted, to the extent of 70%, of cholesterol. The residue, after extraction with ether, was partly soluble in alcohol at 37°. Of the alcoholic extract, part remained insoluble after treatment with ether. This was obtained in the form of a white powder of stearin-like consistency, which swelled on treatment with water, and had m. p. 180—185°. Its analysis indicated a diaminomonophosphatide, similar in its properties to the myelins. Of the ether-soluble portion of the alcoholic extract, the greater part was precipitable by acetone, and of the acetone

precipitate, part was insoluble in hot alcohol, although soluble in ether and chloroform. This was a monophosphatide with the properties of a kephalin. The stromata of sheep's corpuscles contain therefore about 5% cholesterol and 12% phosphatides, of which about half is sphingomyelin, and kephalin is a constituent of the remainder. The blood of normal individuals and of carcinomatous individuals (drawn in the latter case from the cadaver) was examined in a similar manner to that employed in the case of sheep's blood. No essential differences in the chemical composition of the stromata of normal and cancerous individuals could be found, the ethereal extract containing 71·6 and 74% of cholesterol, and the alcoholic extracts 35 and 31% of sphingomyelin. There was isolated, in addition to kephalin, from the acetone precipitate from human blood small quantities of a phosphatide with 3·3% phosphorus and 4·33% nitrogen, which yielded a clear solution in water, but was insoluble in hot alcohol and ether. S. B. S.

Distribution of Ions in the Blood Serum. PETER RONA and PAUL GYÖRGY (*Biochem. Zeitsch.*, 1913, **56**, 416—438).—According to Zuntz and Hamburger, part of the sodium of the serum is non-diffusible, as it is in combination with the proteins. On treatment of the serum with carbon dioxide, part of this sodium should be convertible into sodium hydrogen carbonate. If therefore, serum treated with carbon dioxide is submitted to dialysis (by the compensation method repeatedly used by Rona), the outer liquid should contain more sodium hydrogen carbonate than the dialysate of a serum which has not been so treated. This was actually found to be the case, and the results confirm the statements of Zuntz. The carbon dioxide should, however, convert the serum proteins into a carbamic acid derivative. There would therefore exist in the dialysor sodium salt of a non-diffusible acid. Attention is called to the fact that, according to Donnan's theory (A., 1911, ii, 848), arrived at by thermodynamic considerations, the amount of sodium hydrogen carbonate on both sides of the dialysing membrane will not be the same when equilibrium is established, for on one side there is an electrolytically dissociated substance with a non-dialysable ion. The sodium hydrogen carbonate in the dialysor could not be estimated in a satisfactory manner by incineration. The contents were therefore submitted to ultra-filtration in a Bechhold apparatus, and the filtrate was analysed. The distribution of the chlorine was also investigated, when the [$H^{\cdot}$] concentration of the serum was altered by the addition of acetic acid. In concentration above $H^{\cdot}=10^{-5}$, equilibrium exists with a higher concentration of chlorine inside than outside the membrane, whereas in lower [$H^{\cdot}$] concentrations the reverse is the case. The critical point of change is the isoelectric point, through which the protein changes from the anionic to the cationic state. The Donnan theory is also applicable in this case to the determination of the distribution of the chlorine. S. B. S.

Salts in the Coagulation of Blood. C. GESSARD (*Compt. rend.*, 1913, **157**, 799—802).—A study of the influence of various salts

on the blood of a horse. The amount of salt necessary to prevent coagulation varied with the salt employed, and the plasma obtained could be made to coagulate according to the kind and amount of salt used either by dilution or by addition of a calcium salt, or by addition of serum. Magnesium chloride and sulphate are the most appropriate for the study of these phenomena, since they do not precipitate calcium salts, give no apparent reaction with the saline constituents of blood, and for small differences in weight give different types of plasma. W. G.

The Inactivation of Complement by Mechanical Agitation. HANS SCHMIDT (*J. Hygiene*, 1913, **13**, 291—313).—The complement in serum is inactivated by shaking. This does not seem to be associated with the precipitation of protein, which also occurs. No explanation of the inactivation is at present forthcoming.

W. D. H.

Complement Action in Regard to Surface Tension. HANS SCHMIDT (*J. Hygiene*, 1913, **13**, 314—334).—No relationship between the surface tension and complement action of serum was found.

W. D. H.

The Rate of Elimination of Nitrogen as Influenced by Diet Factors. I. The Influence of the Texture of the Diet. LAFAYETTE B. MENDEL and ROBERT C. LEWIS (*J. Biol. Chem.*, 1913, **16**, 19—36).—A standard diet was arbitrarily selected for dogs, and a constant curve of nitrogen elimination was obtained. This shows a rise reaching a maximum in the second three hours, and then a fall to the initial level early the next day. Delay in elimination is caused by adding indigestible materials, such as mineral oil, vaselin, bone ash, paraffin, filter paper, cork, agar-agar; the effect increases in the order these are enumerated. The last four cause a higher rate of elimination in the later periods. This is attributed to a slower rate of absorption, which in its turn may be produced by (1) rapid emptying of the stomach, and a consequent early exclusion of gastric digestion; (2) the indigestible material may make the digestible material less readily accessible to digestive enzymes; or (3) the final digestion products may be adsorbed by the indigestible substances. Sand gives exceptional results; it causes more rapid elimination of nitrogen during the first six hours. This is not due to increased excretion and reabsorption of digestive juices, for in starvation it has no effect. W. D. H.

The Rate of Elimination of Nitrogen as Influenced by Diet Factors. II. The Influence of Fats and Carbohydrates in the Diet. LAFAYETTE B MENDEL and ROBERT C. LEWIS (*J. Biol. Chem.*, 1913, **16**, 37—53).—Carbohydrates delay the elimination of nitrogen when added to a protein meal; their effect increases in the order: starch, soluble starch, sucrose, dextrose. This may be explained by the tentative suggestion that it is due to the protein-sparing action of carbohydrates. In reference to fats, cottonseed oil delays

the elimination of nitrogen, but lard and "oleo-stearin" hasten it in the early periods. The last-named effect is, however, only due to removal of sucrose from the diet. W. D. H.

The Rate of Elimination of Nitrogen as Influenced by Diet Factors III. The Influence of the Character of the Ingested Protein. LAFAYETTE B. MENDEL and ROBERT C. LEWIS (*J. Biol. Chem.*, 1913, **16**, 55—77).—Extracted meat lowers the rate of nitrogen elimination; the explanation advanced is that extracted meat contains relatively more connective tissue, and therefore is not so digestible. The curves following the ingestion of caseinogen, ovovitellin, edestin, "glidine," and gelatin show no more differences than those noted in the two meat products. Egg-white or albumin and soy bean give different curves due to rate of digestion and absorption, or, in the case of soy bean, to the presence of sucrose. Proteins do not differ materially in their rate of metabolism. The opposite findings of others are discussed. W. D. H.

The Metabolism of Infants During Starvation. ARTHUR SCHLOSSMANN and HANS MURSCHHAUSER [and, in part, KARL MATTISON] (*Biochem. Zeitsch.*, 1913, **56**, 355—415).—The authors, in confirmation of their previous investigations, show that the metabolism during starvation depends on the diet consumed in the period preceding the fast, and that the more nitrogen consumed during the period the greater is the amount of body protein decomposed during the first two or three days of starvation. Similar results were obtained in the case of infants. The breast-fed children metabolise less nitrogen than the artificially fed. There is, however, a marked difference between the metabolism of the two classes during starvation, for whereas the artificially fed children excrete less nitrogen during the period of fast than during the nutrition period, the reverse is the case with the breast-fed infants. In spite of this fact, however, the breast-fed children still excrete less nitrogen during the starvation period than the hand-fed children, and the authors draw the conclusion that the former are more capable of resisting the effects of deprivation of food. The excretion of the acetone substances during starvation was also investigated. The amount excreted rapidly increased in the second day of hunger, running nearly parallel with the increased output of nitrogen in the case of the breast-fed children. In the case of the hand-fed children, the acetone substances increased with diminishing nitrogen output. A few measurements of the respiratory exchanges were also made by the authors. S. B. S.

The Method and Places of Formation of Conjugated Glycuronates in the Organism. JUHO HÄMÄLÄINEN (*Chem. Zentr.*, 1913, ii, 1319—1320; from *Skand. Arch. Physiol.*, 1913, **30**, 196—198).—The small intestine of a rabbit under ether narcosis, after washing, was perfused with Ringer's fluid from the mesenteric artery to the portal vein. α-Santenol and dextrose were then injected into the intestine. After six hours' perfusion, the per-

fusion fluid and intestinal contents were examined, and a non-crystalline substance with the properties of α-santanolglucoside was isolated. Glucoside formation appears to take place therefore in the intestinal wall. S. B. S.

Fat Absorption by the Gastric Mucosa. CHARLES W. GREENE and WILLIAM F. SKAER (*Amer. J. Physiol.*, 1913, **32**, 358—368).—Evidence is adduced that absorption of fats occurs in the stomach of mammals (cats, dogs, rats). The gastric epithelium contains fat even in fasting; this is increased by feeding on fats. The fat in the gland cells, especially in the pyloric region, may be increased by fasting. This has no relation to absorption fat, but is due to mobilisation of the body fat. The observations throughout are histological. W. D. H.

The Procesees of Absorption in the Intestine. N. A. DOBROWOLSKAJA (*Biochem. Zeitsch.*, 1913, **56**, 267—290).—The author discusses the various views as to the method of utilisation of the proteins in the organism, including those of Heidenhain, Hoffmeister, Abderhalden, etc., and attempts by various experimental methods to throw some light on the mechanism. In the first series of experiments, he analyses the serum of portal blood of dogs, estimating the changes of total non-protein nitrogen, and the amino- and peptide-nitrogen produced by the introduction of the chymus obtained from intestinal fistulæ of other animals into the small intestines. No definite results were obtainable by this method, as it was shown that the operative procedure alone, without introduction of digestion products, produced changes in the composition of the serum of the experimental animals. In a second series of experiments, the *in vitro* changes on the amino-nitrogen produced by serum, intestinal extracts, pancreas, etc., on amino-acids and digestion product of proteins, were investigated. The results again lead to no definite conclusions, in some cases indicating synthesis, and in others peptide degradation. In the third series of experiments, an anastomosis was made between the portal vein and the kidneys by the junction of the central end of the *vena lienalis* with the peripheral end of the renal artery. It was assumed that, in the event of introduction of digestion products in the intestine, and a consequent resorption of amino-acids into the portal vein, the excess would be eliminated by the kidneys. To increase the pressure in the kidneys, the portal vein was partly constricted above the junction with the *vena lienalis*. In the majority of cases, the kidney not connected with the portal vein was extirpated. In all of these cases, the animals died. In two cases, when the second kidney was left intact, a certain number of experiments were performed, and the nitrogen of the amino-groups, the hippuric acid, and ammonia nitrogen of the urine excreted were estimated. The introduction of nitrogen into the alimentary tract (by feeding) lead in many cases, especially that of alanine, to an increased amino-nitrogen in the urine. Owing to the fact that the second kidney was intact, these experiments could hardly be considered

satisfactory. In the fourth series of experiments, a portal vein fistula was made according to the method of London and the author, and blood was removed by way of the fistula at various periods after feeding. The results showed a periodic fluctuation in both the portal blood and the blood of the general circulation (removed from the jugular vein). The general result of the experiments is to indicate the difficulty of artificially increasing the amino-nitrogen of the portal vein under conditions approaching the normal physiological. S. B. S.

The Indispensability of Lipoids for Life. The Relation of the Necessary Substances to the Lipoid Extracting Agents. Wilhelm Stepp (*Zeitsch. Biol.*, 1913, **62**, 405—407 Compare A., 1911, ii, 1002).—This is a continuation of the author's previous work on mice. A mixture of lecithin, cholesterol, kephalin, cerebron, and phytin added to a diet freed from lipoids by alcohol-ether extraction, does not supply the missing necessary material. If the primary acetone extract of egg-yolk is added to lipoid-free food, the result is that the necessary material is still lacking; the same is true for the secondary alcoholic extract. But the primary alcoholic extract restores the value of the lipoid-free food. The materials necessary for life are therefore soluble in alcohol, but not in acetone. If the material is extracted with acetone first, part only of the indispensable material goes into solution; the acetone-soluble substances are soluble also in alcohol. Extraction with ether does not remove the indispensable material; fat is therefore for the mouse not indispensable. Extraction of the food with alcohol entirely removes its power to support life. W. D. H.

Are there Substances at Present Unknown in Food-stuffs which are of Importance for the Maintenance of Life? Emil Abderhalden and Arno E. Lampé (*Chem. Zentr.*, 1913, ii, 522—523; from *Zeitsch. gesamte. expt. Med.*, 1913, **1**, 296—354).—As a result of a critical experimental investigation on a broad basis of the work of Suzuki, Shimamura and Odake, and of Funk and others, the authors draw the conclusion that up to the present time there has been no absolute proof of the existence of unknown substances in foods, of general significance, which are essential to the maintenance of life. They do not consider that the action of the so-called oryzanin of the Japanese authors, or of Funk's vitamine, has as yet been definitely established. S. B. S.

The Biological Significance of the Fat-content of Fish, with Special Reference to their Habitat. Osw. Polimanti (*Biochem. Zeitsch.*, 1913, **56**, 439—445).—Attention is called to the fact that during the development of fish embryos, the amount of visible fat diminishes, during which time the habitat gradually alters from that of an organism living on the surface of the water to one living deeper in the sea. It seemed therefore possible that the nectonic fish, which move rapidly about the surface, should contain more fat than the less active, more slowly moving, benthonic fish. Numerous analyses of various species were carried

out, which tend to confirm the above theory, the fat varying from 1·115 to 20·447% of the solid substance. S. B. S.

Proteins of Fish Sperm. ALBRECHT KOSSEL (*Zeitsch. physiol. Chem.*, 1913, **88**, 163—185).—The protamines from the sperm of a number of species of fish have been isolated and investigated. (The figures given are % of total nitrogen.)

Percine from the yellow perch (*Perca flavescens*) contains 85·5% of diamino-acid nitrogen, and 9·8% of monoamino-acid nitrogen, the former being mainly arginine (78·1%) with some histidine (5·6%). No lysine was present. The protamine from the pike perch (*Stizostedion vitreum*) proved to be identical with this.

That from the tunny (*Thynnus thynnus*) (compare Ulpiani, A., 1903, i, 215), which is termed thynnine, contains 80% of arginine nitrogen, no lysine or histidine, and 10% of monoamino-acid nitrogen. The sulphate, like that of other protamines, separates from aqueous solution as an oil. Thynnine also contains tyrosine. *Pelamys sarda* contains a very similar protamine.

The protamine of the sword fish contained 81·5% of arginine nitrogen, and 14% of monoamino-acid nitrogen. Neither histidine nor lysine were present.

The protamine of *Oncorhynchus tschawytscha*, the Chinook salmon (compare A. E. Taylor, A., 1909, i, 344), is identical with the salmine from Rhine salmon (Kossel and Dakin, A., 1904, i, 355, 702).

In the white fish (*Coregonus albus*) the proportions of arginine and monoamino-acid nitrogen are 87·3 and 9·4. In the lake trout (*Salvelinus*) they are 88·9 and 7·1, whilst in *Esocine*, the protamine of the pike (*Esox lucius*), they are 86·3 and 11·3.

In general, these protamines contain two molecules of arginine to one molecule of monoamino-acid—in a few protamines the proportion of monoamino-acids is larger. The protamines are thus to be expressed by the formula a_2m, where a is arginine, or $(alh)_2m$, when all three diamino-acids are present, the proportion of diamino-acid being again as 2 to 1.

A table is given of the known protamines and their formulæ. E. F. A.

The Lipoids of Nervous Tissue. CESARE SERONA and ANOTOINETTE PALOZZI (*Chem. Zentr.*, 1913, ii, 1064—1065; from *Arch. Farm. sperim.*, 1913, **15**, 375—384).—The composition of the brain (white and grey matter) of ox and calf was as follows: 14·25—16·13‰ cholesterol and the esters of cholesterinolic and palmitic acids, 39·8—44·1‰ oleic acid and palmitic acid lecithins. 14·6—14·8‰ cerebrin, and 3·76—5·8‰ homocerebrin or cerasin. To separate the constituents, the following process was employed. The brain was extracted with 5—6 times its weight of a mixture of equal parts of alcohol and ether. From the residue a substance could be extracted with hot alcohol with m. p. 164—165°, which had the properties of homocerebrin or cerasin. The alcohol-ether extract yielded, after evaporation of the ether, a flocculent mass *A*, and the alcoholic residue on evaporation, a waxy mixture *B*.

Each of these fractions was treated successively with cold acetone, cold ether, and hot alcohol. The acetone extract was fat-free, and contained, besides some phosphatic lipoids and cerebrin, which became insoluble on solution and reprecipitation with acetone, chiefly cholesterol and its fatty esters. The ethereal extract could be separated into two fractions, one, insoluble in cold alcohol, yielding a substance corresponding with Thudichum's and Koch's kephalin, which appears, on further investigation, to be an impure lecithin mixed with cerebrin, and a soluble fraction, consisting also chiefly of impure lecithin mixed with cerebrin. The alcoholic extract was also separated into fractions soluble and insoluble in cold alcohol. The former consisted of cerebrin, m. p. 190—192°, which on hydrolysis yielded a fatty acid, m. p. 74—75°, presumably cerebrotinic acid, and a reducing sugar with $[\alpha]_D^{23}$ +27·5°, and a substance which is possibly galactosamine. The part soluble in cold alcohol, m. p. 160—165°, is apparently impure homocerebrin or cerasin. S. B. S.

Influence of Activity on Automatic Rhythm in Heart Muscle. GEORGE R. MINES (*Proc. physiol. Soc.*, 1913, xiii; *J. Physiol.*, 47).—If a frog's or mammal's heart is made to beat faster, the subsequent automatic rhythm is slowed; in the octopus the reverse occurs. In both cases, forced activity leads to formation of acid, but in different hearts, and different parts of the same heart, the optimum hydrogen ion concentration is different. In some cases the increase will be towards this value, in others away from it.
W. D. H.

Hydrogen Ion Concentrations Limiting Automaticity in Different Regions of the Frog's Heart. (Miss) DOROTHY DALE and C. R. A. THACKER (*Proc. physiol. Soc.*, 1913, i—ii; *J. Physiol.*, 47).—The different heart chambers develop rhythm with varying degrees of hydrogen ion concentration. The sinus will beat in solutions which are too acid for the auricle, and the same holds between auricle and ventricle. Similar differences appear on the alkaline side. The actual figures are given in the paper. W. D. H.

Synthetic Sugar Formation in the Artificially Perfused Liver. GUSTAV EMBDEN, ERNST SCHMITZ and MARIA WITTENBERG (*Zeitsch. physiol. Chem.*, 1913, **88**, 210—245).—The perfusion fluid employed was Ringer's solution, containing in it dog's blood-corpuscles washed by centrifugalising. If the liver (dog) is freed from glycogen by phloridzin poisoning, the perfusion leads to a slight but constant formation of sugar. If then dihydroxyacetone is added, the amount of sugar formed (dextrose) is increased. The addition of *dl*-glyceraldehyde to the perfusing fluid increases the sugar formation greatly; this sugar is in part *d*-sorbose. The aldehyde appears to be directly transformed into the sugar with previous rupture into short carbon chains. Glycerol forms dextrose less than the two trioses. W. D. H.

Formation of Acetoacetic Acid from Acetic Acid [in the Liver]. GUSTAV EMBDEN and ADAM LOEB (*Zeitsch. physiol. Chem.*, 1913, **88**, 246—258).—A study of the formation of acetoacetic acid

in the liver indicates that it is not formed from acetic acid by oxidative changes. The presence of *n*-valeric acid or of propionic acid prevents its formation from acetic acid. Formic acid is without influence, and is but little attacked on passing it through the liver. *dl*-Lactic acid has less effect on the reaction than propionic acid.

The conversion of acetic acid into acetoacetic acid is greatly retarded when the liver is full of glycogen. The addition of glycollic acid to the blood stream increases the formation of acetoacetic acid in the liver, although to a less extent than acetic acid.

E. F. A.

The Effect of Pituitary Extract on Renal Activity. C. E. KING and O. O. STOLAND (*Amer. J. Physiol.*, 1913, **32**, 405—416).—The view is disputed that pituitrin directly stimulates the renal epithelium; the vascular changes (vaso-dilatation) are considered sufficient to account for the diuresis. W. D. H.

The Heat-production of Fatigue and its Relation to the Production of Lactic Acid in Amphibian Muscle. RUDOLPH A. PETERS (*J. Physiol.*, 1913, **47**, 243—271).—By a modification of A. V. Hill's calorimeter it was found that the heat produced by the indirect stimulation of frog's muscles until fatigue set in has a maximum value of about 0·9 cal. per gram of muscle. The heat liberation is roughly exponential, and about 70—80% of it is liberated in the first two minutes. The figure 0·9 is about half of that obtained in chloroform rigor. No processes other than contraction arise in the production of rigor. The lactic acid figures agree with those of Fletcher and Hopkins; heat production and lactic acid liberation are intimately associated. W. D. H.

The Presence in the Vascular Walls of a Ferment Setting Free a Reducing Sugar at the Expense of the Virtual Sugar of the Blood, and Decomposing Phloridzin. RAPHAEL LÉPINE and RAYMOND BOULUD (*Compt. rend.*, 1913, **157**, 627—628. Compare this vol., i, 1274).—The experiments show the presence of a ferment in the vascular walls of the kidneys, lungs, and aorta, capable of setting free a reducing sugar in the blood, a function previously ascribed to the liver alone. The ferment is also capable of partly hydrolysing phloridzin. W. G.

Amylogenesis and its Relation to Glycolysis in the Animal Organism. CESARE PADERI (*Chem. Zentr.*, 1913, ii, 1316; from *Arch. Farm. sperim.*, 1913, **16**, 54—96).—From his own results and those of other investigators, the author draws the conclusion that glycogen formation is a necessary preliminary process in the utilisation of sugar in the organism, and that a disturbance of this function results in diabetes mellitus. For the treatment of this condition, therefore, substances must be employed which assist the glycogen formation. Extract of muscles and of pancreas, both alone or combined, were found to be incapable of degrading dextrose at 37°. Disappearance of this substance under these

...tions can be attributed to bacterial action. Lactic and acetic ...ds were formed from the sugar under the combined action of ...ncreas extract and micro-organisms. The formation of these ...ds accounts for the fact that the addition of dextrose inhibits ...far-reaching putrefaction of pancreas. No alcohol could be ...ected as a result of the combined action of pancreas and bacteria ...sugar. A fasting animal exhibited appreciable formation of ...cogen in the liver. Addition of extract of pancreas did not ...hibit sugar formation in the transfusion of a surviving liver.

S. B. S.

A Comparison of the Observed and Computed Heat Production of Cattle. HENRY PRENTISS ARMSBY (*J. Amer. Chem. Soc.*, 1913, **35**, 1794—1800).—Experimental evidence that in the case ...man and carnivora the usual equivalence exists between chemical ...ergy, heat energy, and mechanical energy, is already forthcoming, ...t hitherto such investigations have not, as a rule, included an ...xamination of herbivorous animals.

The present paper gives an account of results obtained during the last decade on cattle (steers), and in the aggregate of fifty-seven experiments the observed heat production differs from the computed by only 0·4%.

D. F. T.

Constituents of Animals Fats. The Fat of Cervus elaphus. ...KLIMONT and E. MEISL (*Monatsh.*, 1913, **34**, 1489—1492).—A lard from the red deer, with the following constants, has been examined: D 50°, 0·9066, acid number 20·5, saponification number 203·5, iodine number 19·3, m. p. 48° (Pohl), solidification point ...5°. The fat was recrystallised eleven times from hot acetone, when β-palmityldistearin, m. p. 62·5—63·5°, was obtained (compare Bömer and Limprich, this vol., i, 442).

J. C. W.

The Organic Substance in the Skeletal Tissues of Anthozoa. IV. Isolation and Identification of Bromogorgonic Acid. CARL TH. MÖRNER (*Zeitsch. physiol. Chem.*, 1913, **88**, 138—154. Compare A., 1907, ii, 283; A., 1908, ii, 310).—3:5-Dibromo-*dl*-tyrosine has been identified as a product of the hydrolysis of *Primnoa* gorgonin with barium hydroxide. This is the first organic bromo-compound obtained by the hydrolysis of a naturally occurring protein. The whole of the bromine present in the gorgonin molecule is not dibromotyrosine. Other products of the hydrolysis of gorgonin are tyrosine, glycine, alanine, leucine, aspartic, glutamic, and oxalic acids.

E. F. A.

The Secretion of Cerebro-spinal Fluid. WALTER E. DIXON and WILLIAM D. HALLIBURTON (*J. Physiol.*, 1913, **47**, 215—242).—An intravenous injection of an extract of the choroid plexuses (choroid glands) produces an increased secretion of cerebro-spinal fluid, as tested by its rate of outflow through a cannula. The active principle is thermostable, soluble in water and in alcohol, and does not pass the pores of a Chamberland filter. Other effects of the

injection are increase of respiration, and a slight fall of blood pressure. Extracts of brain produce the same effect, but less markedly; no other animal extracts act in the same way. Probably, as a result of cerebral activity, some waste product acts as a hormone to stimulate the activity of the choroid cells, and from the richness of the cerebro-spinal fluid in carbon dioxide, it is suggested that one function of the fluid may be to enable the brain to get rid of this material. Reasons are given why this hormone is considered to act on the gland cells and not on secretory nerves. The hormone in question is not found in the cerebro-spinal fluid itself except in cases where catabolism is in excess, as in degenerative processes of the central nervous system.

Other agents which produce an increase of the fluid are excess of carbon dioxide in the blood, and drugs which interfere with respiration. The volatile anæsthetics have a similar action; these may act by interfering with oxygenation or by altering the physical condition of the secreting cells. A large number of substances were investigated, but all the remainder gave negative results, if respiratory and vascular effects were excluded. W. D. H.

The Comparative Composition of Human and Cow's Milk. EDWARD B. MEIGS and HOWARD L. MARSH (*J. Biol. Chem.*, 1913, 16, 147—168).—Human milk differs from cow's milk in three important ways. It contains more lactose, less protein, and more substances of unknown nature. The following figures are averages in percentages of the whole milk:

	Fat.	Lactose.	Protein.
Human milk..............	2 to 4	6 to 7·5	0·7 to 1·5
Cow's milk	2 ,, 4	3·5 ,, 5	2·5 ,, 4

The unknown constituents are soluble in alcohol and ether; they contain little or no nitrogen, and are of importance as food. Some are crystalline, and the crystalline form of one is figured and described at length. (This contains sulphur, but is free from nitrogen.) They are most plentiful in early human milk (1%); as lactation proceeds they sink to 0·5%. Cow's milk at the latter period contains 0·3%. The paper contains analytical tables, and descriptions of methods. Much of the work was done by the late Arthur V. Meigs. W. D. H.

The Soluble Caseins of Milk. LÉON LINDET (*Bull. Soc. chim.*, 1913, [iv], 13, 1001—1006. Compare this vol., i, 1116).—Further experiments are quoted in support of the author's views as to the presence of an α- and β-caseinogen in milk and the relationship between them. The sum of these two substances present is fairly constant in milk, but the proportions of each are very variable. W. G.

Solubility of the Proteins of Milk in the Elements of the Serum. Reduction of their Solubility under the Influence of Calcium Chloride. LÉON LINDET (*Bull. Soc. chim.*, 1913, [iv], 13, 929—935). —The soluble proteins of milk include casein (distinguished as

α-casein, having $[\alpha]_D$ −116°, and a second, called β-casein, which differs only in specific rotation, $[\alpha]_D$ −30°. Milk serum, from which all the proteins had been removed by means of phenol, on evaporation and incineration yielded ash of the following composition, expressed in grams per litre of milk: alkali chlorides, 1·949; alkali citrates (calculated from the carbonate found), 0·765; alkali phosphates, 0·514; calcium phosphate, 0·638; magnesium phosphate, 0·458; iron and aluminium phosphates, 0·108; calcium sulphate, 0·341; undetermined, 0·387. An artificial serum containing lactose, 5; sodium chloride, 0·2; sodium citrate, 0·08; and sodium phosphate, 0·05 per cent., can dissolve 3·456 grams of casein per litre, and probably as much more of the β-casein. In milk, probably all the β-casein is in solution, and about 10% of the α-casein, the rest of the latter being in suspension. The addition of calcium chloride to milk before coagulation by rennet increases the nitrogen and phosphate content of the coagulum and accelerates the action, due to its converting the sodium salts into insoluble calcium salts, and thereby destroying the solvent action of the former on the casein. T. A. H.

Psychic Hyperglycæmia in Rabbits. IVAN BANG (*Zeitsch. physiol. Chem.*, 1913, **88**, 44—46).—Hirsch and Reinbach (*ibid.*, 1913, **87**, 122) have described a hyperglycæmia and glycosuria in rabbits as the result of fright. The non-recognition of this condition produced by psychical causes renders much work on the general subject untrustworthy. The existence of such a psychic condition in rabbits and other animals is confirmed in the present paper.
W. D. H.

Pentosuria from the Chemical Point of View. ERNST ZERNER and RUDOLFINE WALTUCH (*Monatsh.*, 1913, **34**, 1639—1652).—In most cases of pentosuria which have been investigated, optically inactive urines have been encountered, from which osazones apparently corresponding with *i*-arabinose or *l*-arabinose have occasionally been isolated.

Two new cases of pentosuria have now been examined. The urines were inactive, which is taken as an indication of the absence of *l*-arabinose, since this has a very high specific rotation. The osazone obtained had m. p. 162—163°, and a small *d*-rotation, which was insufficient to distinguish it from *d*-arabinosazone. Diphenylmethanedimethyldihydrazine (Braun, 1910, i, 525) gave no indication of arabinose. A mixture with an equal weight of *l*-xylosazone had m. p. 208—210°, whereas *i*-xylosazone has m. p. 210—215° (Fischer, A., 1894, i, 566). The osazone from these urines is therefore *d*-xylosazone, and very probably the pentose is *d*-xylose. Further experiments are being carried out definitely to determine the nature of the sugar. J. C. W.

The Sugar in Pentosuric Urine. CARL NEUBERG (*Biochem. Zeitsch.*, 1913, **56**, 506—507).—Zerner and Waltuch (preceding abstract) have maintained that the sugar isolated by them in a

case of pentosuria was *d*-xylose, as the mixture of its osazone with that of the corresponding *l*-derivative has a higher melting point than the pure substance. A mixture of the *l*-form of osazone with the osazone obtained from the urine of the cases of pentosuria of the author did not produce a corresponding rise in the melting point. The author does not see, therefore, any reason to suppose that the sugar in his case is other than the *dl*-arabinose, as originally suggested. It is conceivable that various forms of pentosuria exist. S. B. S.

Physiological Action of Colloidal Carbon. Guido Izar and C. Patanè (*Biochem. Zeitsch*, 1913, **56**, 307—318).—The so-called mellogen, produced by the disintegration of a carbon anode by a galvanic current, was used in these experiments. It can be dispersed in water made slightly alkaline by sodium hydroxide, which mixture is afterwards neutralised by passing in carbon dioxide and heating. This preparation has no influence on the total autolysis of the liver. It increases the amount of uric acid formed by autolysing ox-spleen and liver, and inhibits the uricolytic action of ox-kidneys and washed pulp of dog's liver. Intravenous injections of largo quantities into rabbits, white rats, pigeons, etc., produce dyspnœa, but only a few of the animals succumb. The intravenous injection has no appreciable effect on body temperature (rabbits), but increases the amount of carbon dioxide in expired air (as compared with control injection of distilled water). The amount of increase is approximately proportional to the amount of mellogen injected. S. B. S.

Action of Colloidal Sulphur on Autolysis. Antonio Fagiuoli (*Biochem. Zeitsch.*, 1913, **56**, 291—294).—Colloidal sulphur increases the autolysis of liver tissue (ox, dog, and monkey), and to a still larger extent that of tumour tissue (rat sarcoma and human liver carcinoma). S. B. S.

Pharmacological Action of Ethyl Alcohol on the Isolated Mammalian Heart at Different Temperatures. Giuseppe Brandini (*Chem. Zentr.*, 1913, ii, 524; from *Arch. Farm. sperim.*, 1913, **15**, 178—192, 193—212).—The experiments were carried out on a rabbit's heart in a Langendorff perfusion apparatus. At normal temperatures the alcohol in small doses (1 in 50,000—1,150,000) exerts a stimulant action, in medium doses, the heart activity is depressed, but in higher concentrations ($30^{0}/_{00}$) the action is toxic. At lower temperatures (33°) the effect is weaker, and higher concentrations of alcohol are required to produce the same effects described as resulting at 37°. S. B. S.

The Scission of the Benzene Ring in the Animal Body. II. Behaviour of Muconic Acid and Benzene in Liver-perfusion Researches. Marie Hensel and Otto Riesser (*Zeitsch. physiol. Chem.*, 1913, **88**, 38—43).—When muconic acid is added to a fluid employed for perfusing the liver, the amount of acetone formed

... that organ is greatly increased, it may be fourfold. No certain result was obtained by perfusing the liver with benzene; this substance is strongly toxic. W. D. H.

The Conjugated Excretion Products of Bromobenzene and p-Iodophenol. Erberto Angelo Rabbeno (*Chem. Zentr.*, 1913, ii, 1070; from *Arch. Farm. sperim.*, 1913, **15**, 535—546).—It was presumed that it should be possible, by the estimation of the total sulphur, the conjugated sulphuric acid, and the rotation of the urine of dogs, to which bromobenzene and *p*-iodophenol had been administered *per os*, to ascertain whether the halogen derivatives of benzene undergo conjugation with glycuronic acid as well as with cystine and sulphuric acid. It was found as a result of the experiments that the bromine derivative is excreted conjugated only with cysteine and sulphuric acid, whereas the iodo-derivative is excreted conjugated with glycuronic and sulphuric acids, but not with cysteine. S. B. S.

The Influence of the Administration of Creatine and Creatinine on the Creatine Content of Muscle. Victor C. Myers and Morris S. Fine (*J. Biol. Chem.*, 1913, **16**, 169—186).—The subcutaneous administration of creatine to rabbits causes a small increase in the creatine content of muscle (about 5% in five experiments). This is quite insufficient to account for the creatine, which does not reappear in the urine. The administration of creatinine exerts a similar effect, the creatine content of the muscles being 6% above the normal, an amount sufficient to account for the creatinine which was not eliminated by the kidneys. This apparent increase in the muscular creatine was not due to a retention of unchanged creatinine. Of the creatine given, 25—80% (the quantity depending on the amount injected) reappeared in the urine unchanged, whilst 2—10% was eliminated as creatinine. When creatinine was administered, 77—82% (average 80%) reappeared in the urine, and no elimination of creatine was detected. W. D. H.

Narcosis and Oxygen Consumption. Jacques Loeb and Hardolph Wasteneys (*Biochem. Zeitsch.*, 1913, **56**, 295—306).—The authors discuss the relationship between inhibition of oxidation and narcosis. When the embryos of *Fundulus* are not narcotised, they respond by rapid movement to a stimulus of $N/25$-hydrochloric acid. It was found that they only become insensitive to this stimulus when their oxidation rate has been reduced to 1/14 of the normal value by potassium cyanide; a reduction by this method to 1/9 is without influence on their response to the stimulus. On the other hand, they become unresponsive to chloroform treatment, without any appreciable reduction of the oxidation rate. Ethyl ether and butyl alcohol can produce insensitiveness to the strongest stimuli with the diminution of the oxidation rate by only 26%. Medusæ loose their mobility and reactivity to stimuli by direct reduction of oxidation by potassium cyanide only

when this reduction is 3—6 times as great as that which results when the motility and reactivity are destroyed by ethylurethane. The conclusion is drawn that narcosis cannot be due directly to reduction of oxidative capacity, and that the latter is a result either of inactivity of the tissues due to narcosis, or it is a secondary action of the narcotis, which stands in no direct relationship to the narcosis itself. S. B. S.

Biological Oxidation of Certain Glucosides. JUH. HÄMÄLÄINEN (*Chem. Zentr.*, 1913, ii, 1319; from *Skand. Arch. Physiol.*, 1913, **30**, 187—190).—After injection of the glucosides of certain terpene alcohols, the corresponding glycuronates appear in the urine. There is therefore no preliminary scission of the glucoside into sugar and alcohol, for neither in the blood nor in the organs could any terpene be detected. On the contrary, both glycuronate and the corresponding glucoside could be found. The facts confirm the theories of Fischer and Piloty and of Sundvik on the formation of conjugated glycuronates in the organism. Furthermore, more glycuronate is excreted after administration of the glucoside than after administration of the free substance. S. B. S.

The Influence of Certain Quinoline and Naphthaquinoline Derivatives on the Excretion of Uric Acid. RICCARDO LUZZATO and RICCARDO CIUSA (*Chem. Zentr.*, 1913, ii, 1318—1319; from *Arch. Farm. sperim.*, 1913, **16**, 6—40).—The following derivatives were investigated: 2-*p*-methoxyphenylquinoline-4-carboxylic acid, 2-*p*-dimethylaminophenylquinoline-4-carboxylic acid, 6-amino-2-phenylquinoline-4-carboxylic acid, 3-phenyl-β-naphthaquinoline-1-carboxylic acid, 2-*p*-dimethylamino-β-naphthacinchonic acid, 2-phenyldihydro-β-naphthaquinoline-4-carboxylic acid, 2-*o*-hydroxylphenyl-β-naphthacinchonic acid, 3-phenyl-β-naphthaquinoline, and 2-phenylcinchonic acid (atophan). Of these it was found that 3-phenyl-β-naphthaquinoline-1-carboxylic acid (the so-called diapurin) and atophan caused an intense excretion of uric acid, the action of the latter being somewhat less than that of the former. It caused, however, no turbidity of the urine, and was better tolerated, and a dose of 5 grams caused no bad symptoms in a dog of 12 kilos. weight, and could be taken by a man in doses of 2 grams for several days without ill effects. The action of diapurin is attributed to the mobilising effects on the uric acid, which already exist in the organism as a result of purine degradation, as the increased excretion of the acid is not accompanied by an increased phosphoric output, which should result if the nucleins are broken down. Furthermore, the increased output of uric acid ceases two or three days after administration of the drug. The particular action on the uric acid is due to the presence of a phenyl group in the 2-position, the quinolinecarboxylic acid group being inactive. The action is neutralised by the presence of the methoxyl and amino-groups in the 6-position. On the other hand, 2-phenyl-6-methylquinoline-4-carboxylic acid (paratophan) and 8-methoxy-2-phenylquinoline-4-carboxylic acid (isatophan) are fairly active. The introduction of the OH

NMe_2 or OMe group into the 2-phenyl ring inhibits or weakens the action on uric acid. As hydroxyphenylquinoline-4-carboxylic acid is, according to Sk'orczewski and Sohn, a degradation product of atophan, the latter appears to exert its influence before oxidation. The reduction of the pyridine ring destroys or weakens the action. The general methods of Doebner, Kuntze, Lachs, and Steinert were employed in the preparation of the compounds, and the following substances were obtained: 2-p-*anisylquinoline-4-carboxylic acid*, m. p. 217°; 2-*dimethylaminophenylquinoline*-4-*carboxylic acid*; [illegible] 2-*phenylquinoline-4-carboxylic acid*, m. p. 160° (decomp.).

S. B. S.

The Behaviour of Certain Rhamnosides in the Animal Body. MARIO GARINO (*Zeitsch. physiol. Chem.*, 1913, **88**, 1—8).—Rutin, quercitrin, hesperidin, and hesperetin, after intravenous or oral administration, pass through the animal organism, and are excreted almost entirely unchanged. Hydrolysis of these substances appears to occur either not at all, or in the merest traces, in the body.

W. D. H.

The Action of Strophanthin on the Excised Frog's Heart. A. J. CLARK and GEORGE R. MINES (*Proc. physiol. Soc.*, 1913, vii—viii; *J. Physiol.*, **47**).—The effect of perfusing the heart with one part of strophantin in a million of Ringer's fluid is at first beneficial, and later toxic. The observations were made on the mechanical activity of the ventricle, the length of the A.V. interval, and on the electrical concomitant of activity.

W. D. H.

Mechanism of the Biological Action of the Röntgen Rays. EUGEN PETRY (*Biochem. Zeitsch.*, 1913, **56**, 341—352).—The author has investigated the influence of Röntgen rays on the toxicity of various metals, following a similar line of research to that of Tappeiner and his pupils on the sensitising influence of eosin on actinic rays. Amœbæ obtained from hay-infusion were used as the objects of experiments, and these were submitted to the action of uranium nitrate, sodium tungstate, zinc sulphate, and colloidal zinc sulphide in the dark, in the presence and the absence of Röntgen radiation. As a result, it was found that the rays had no appreciable effect in increasing the toxicity of the metals. Compounds were purposely chosen which fluoresce when submitted to radiation. The rays exerted no action on the sensitising activity. Experiments were also carried out to ascertain whether organs which are highly sensitive to Röntgen rays contain substances which act as light-catalysts for these rays. Testicles and lymph glands were chosen, and the effect of radiated and unradiated extracts on hæmolysis, the mobility of amœbæ, and the milk-clotting by rennin, were investigated. The results were negative, and the author draws the conclusion that no substances have been discovered which act as catalysts for the Röntgen rays in the same way that eosin acts as catalyst for actinic rays.

S. B. S.

Purine and Xanthine Bases as Intermediary Products in Poisoning by Nucleoproteins. HENRI DE WAELE (*Chem. Zentr.*, 1913, ii, 519—520; from *Zeitsch. Immun. expt. Therapie*, 1913, 18, i, 410—422).—Just as, according to the author, the proteins use the amino-acids as intermediary products in developing their thromboplastic action, the nucleoproteins act by intermediation of the purine bases. Thus nucleoproteins, otherwise harmless, can be rendered toxic by degradation of their molecule, or by the addition to them of degradation products, or even amino-acids. Under these conditions, curves were obtained similar to those described by the author for proteins, showing, in an oscillatory manner, thromboplastic and antithrombic phases. The first of these is short, and may be overlooked. The nucleins produce a strong antithrombic secretion. The antithrombic phase is of short duration, but produces a distinct, although short-lasting, immunity. The nucleoproteins can be activated either by purines (affecting the nucleic acid part of their molecule) or by amino-acids (affecting the protein part). Nucleohistones, owing to the presence of the histone group, are directly toxic. For many nucleoproteins, such as those from the thymus, animals are directly anaphylactic, in the same way that carnivora are sensitive to peptones. S. B. S.

The Removal of the Poisonous Properties of Protein Cleavage Products by Substitution of the Cyclic Nucleus. GEORGE BAEHR and ERNST P. PICK (*Arch. expt. Path. Pharm.*, 1913, 74, 73—91).—The proteins of horse- and ox-serum yield, on gastric digestion, poisonous products. But if these proteins are iodised, nitrited, or diazotised, the products of pepsin digestion no longer produce "peptone-shock," causing neither fall of arterial pressure nor loss of coagulability in the blood. The iodine, nitro- and diazo-groups in question enter the cyclic nucleus of the protein molecule.
W. D. H.

Nature of the Coagulant of the Venom of Echis carinatus, a Small Indian Viper. J. O. WAKELIN BARRATT (*Proc. Roy. Soc.* 1913, [*B*], **87**, 177—190).—The effect of the intravenous injection of thrombokinase is essentially different from that of injection of thrombin. The latter causes an abundant intravascular formation of fibrin and a reduction of the amount of fibrinogen in the circulating fluid. Little or no fibrinogen is removed after the injection of thrombokinase, which thus has an essentially different action on blood plasma than on a solution of fibrinogen *in vitro* in presence of calcium chloride, which it causes to coagulate. The coagulant of viper venom, as exhibited by its effect in causing intravascular separation of fibrin when injected into the blood-stream and also indicated by its behaviour when heated, is a thrombin and not a thrombokinase. E. F. A.

Chemistry of Vegetable Physiology and Agriculture.

Biochemistry of Micro-organisms. VIII. Fermentation of Formic Acid by Bacillus Plymouthensis in a Medium of Constant Composition. Hartwig Franzen and Fritz Egger (*Zeitsch. physiol. Chem.*, 1913, **88**, 73—102. Compare this vol., i, 322; A., 1912, ii, 669).—Further data are given obtained from experiments with *B. Plymouthensis*, made in the same way as previously with *B. kiliense* and *B. prodigiosus*. The results show the same divergence in different series of cultures. *B. Plymouthensis* ferments formic acid during the first twenty-four hours. The maximum amount of formic acid fermented was 9·95% at 17°, 16·8 and 26·47% at 21°, and 22% at 27°. No general conclusions are drawn. E. F. A.

Chemistry of Bacteria. II. Sakae Tamura (*Zeitsch. physiol. Chem.*, 1913, **88**, 190—198).—*Mycobacterium laticola* contains the same organic constituents whether it is grown on nutritive bouillon or on a medium lacking protein. The aromatic units in its composition are formed in quantity when only short open-chain carbon compounds are supplied as food—for example, lactic acid, glycerol, asparagine.

The inorganic constituents of the cells of *Bacterium tuberculosis* or of *Mycobacterium laticola* undergo considerable quantitative variation according to the nature of the environment in which the culture is made. E. F. A.

Violet Colouring Matter and its Production by a Certain Bacterium. W. J. Hartley (*Sci. Proc. Roy. Dubl. Soc.*, 1913, **14**, 63—73).—The pigment of a bright, violet bacterium obtained from a creamery water has been examined. The pigment turns green with acid, blue with alkali; it does not dye silk. The absorption spectrum has been characterised; it has no bands in the ultra-violet, absorbs continuously the rays in the red less refrangible than λ 6600, and transmits nearly all the rays from λ 6600 to λ 6430. The cultures, when macerated, gave a positive test with picrate paper for hydrogen cyanide. E. F. A.

Influence of Radioactivity on Nitrogen-fixing Micro-organisms or on those Transforming Nitrogenous Substances. Julius Stoklasa (*Compt. rend.*, 1913, **157**, 879—882).—Air activated by pitchblende has a markedly favourable influence on the fixation of atmospheric nitrogen by *Azotobacter chroococcum*, the influence being slightly more favourable with weak radioactive intensity than with a stronger intensity. On the other hand, the transformation of organic nitrogen into ammoniacal nitrogen and the fixation of free nitrogen is much weaker in solutions submitted to the influence of β- and γ-rays than in control solutions.

Soil submitted to air charged with radium emanations showed an increased nitrogen content of 0·021% over the control sample. The reduction of nitrates by denitrifying bacteria is considerably lessened under the influence of radium emanation, although there is ample development of the denitrifying bacteria. W. G.

Butylene-glycol Fermentation of Dextrose by Staphylococci and Tetragenes. M. LEMOIGNE (*Compt. rend.*, 1913, 157, 653—655. Compare A., 1912, ii, 1199).—Staphylococci and tetragenes only attack carbohydrates slowly, and do not develop unless they have an abundant supply of organic nitrogenous food. The products of the fermentation of the sugar are dimethyl diketone, acetylmethylcarbinol, and butylene $\beta\gamma$-glycol. W. G.

The Optical Behaviour of Yeast Maceration Juice. CARL NEUBERG and P. ROSENTHAL (*Biochem. Zeitsch.*, 1913, 56, 498—500).—The maceration juices from Lebedev's preparations were found to vary when freshly prepared from $-0·10°$ to $-0·42°$ in optical rotation. On keeping, the optical rotation of the juices diminished in some cases, whereas in others it increased. S. B. S.

Osmotic Pressure and Electrical Conductivity of Yeast, Beer, and Wort. HENRY H. DIXON and WILLIAM R. G. ATKINS (*Sci. Proc. Roy. Dubl. Soc.*, 1913, **14**, 9—12).—Pressed yeast gives higher values than wort, both in osmotic pressure and electrical conductivity. Comparing beer and wort, it is shown that whilst the electrical conductivity remains the same, the osmotic pressure becomes three times as great during fermentation. E. F. A.

Extraction of Zymase by means of Liquid Air. HENRY H. DIXON and WILLIAM R. G. ATKINS (*Sci. Proc. Roy. Dubl. Soc.*, 1913, **14**, 1—8).—Immersion of yeast in liquid air from ten to fifteen minutes renders the protoplasm permeable. On thawing, the yeast liquefies, and after centrifuging, the sap of the cells is obtained as a faintly opalescent, brown liquid. This contains zymase in as active a form as that prepared by Lebedev's maceration method. The amount of zymase extracted may be increased by dilution and maceration. The sap is practically free from glycogen, and does not show autofermentation.

The sediment froths actively, due to hydrolysis of the glycogen in the cells and fermentation of the sugar formed. E. F. A.

The Complete Hydrolysis of Yeast Albumin. HANS PRINGSHEIM (*Woch. Brauerei*, 1913, **30**, 399—400).—The hydrolysis of yeast furnished the following compounds, which were obtained by distillation in the form of esters (Fischer's method). The esters obtained from leucine and valine were the chief product: those from proline, phenylalanine, and glutamic acid were obtained in small quantities; the presence of serine is considered questionable, whilst alanine and glycine were not apparently present.

F. M. G. M.

Influence of Acids on Alcoholic Fermentation. M. ROSENBLATT and (Mme.) M. ROSENBLATT (*Bull. Soc. chim.*, 1913, [iv], **13**, 924—929. Compare A., 1909, ii, 752; 1910, ii, 643; Johannesohn, this vol., i, 143).—None of the acids tried has any accelerating action on the activity of yeast, and each of them begins to retard the activity at the concentrations quoted: Hydrochloric ($M/6000$), formic ($M/5000$), acetic ($M/300$), propionic ($M/250$), butyric ($M/200$); sulphuric ($M/6000$), tartaric ($M/1000$); phosphoric ($M/5000$), citric ($M/3000$). Potassium hydrogen sulphate behaves similarly. The following salts accelerate the activity, and the optimal concentrations are quoted: Potassium hydrogen oxalate ($M/200$), dipotassium hydrogen citrate ($M/10$), potassium dihydrogen citrate ($M/5$), sodium dihydrogen tartrate ($M/4$), potassium dihydrogen phosphate ($M/3$). T. A. H.

Formation of Acid by Fermentation. ED. MOUFANG (*Zeitsch. f. ges. Brauwesen*, 1913, **36**, 297—299).—Dilute solutions of dextrose, lævulose, maltose, and sucrose were treated with yeast in the presence of malt, and the acids formed subsequently estimated by methods which have been described by Mösslinger. F. M. G. M.

Reduction of Chloral Hydrate by Yeast During Alcoholic Fermentation. CARL J. LINTNER and H. LÜERS (*Zeitsch. physiol. Chem.*, 1913, **88**, 122—123).—Living yeast in the act of fermenting sucrose reduces added chloral hydrate to trichloroethyl alcohol. E. F. A.

The Uselessness of Zinc for the Culture of Aspergillus niger. CHARLES LEPIERRE (*Compt. rend.*, 1913, **157**, 876—879).—*Aspergillus niger* will grow on a culture medium, free from all traces of zinc, providing the ratio, volume of liquid/surface exposed, is always greater than 2. If this ratio falls below 2, however, then the maximum growth is never obtained. This explains the difference between the author's results and those of Javillier (compare A., 1908, ii, 317), who grew the mould on liquid where the ratio v/s was 1·5. W. G.

Polyatomic Alcohols as Sources of Carbon for Lower Fungi. RAY E. NEIDIG (*J. Biol. Chem.*, 1913, **16**, 143—145).—Methyl alcohol and ethylene glycol are not capable of producing normal cultures of *Aspergillus* and other moulds when they are introduced into Czapek's medium in place of sugar. Glycerol is readily available, and gives cultures as good as when sucrose is employed. With increasing carbon, the availability does not increase; adonitol, for example, does not compare favourably with glycerol or even erythritol, and two of the hexatomic alcohols failed to yield cultures equal to those on glycerol. No connexion between availability and carbon asymmetry could be established. There may, however, be some relation between availability and the nature of the intermediate oxidation products, since all the substances which are available, including glycerol, yield oxidation products containing one or more asymmetric carbon atoms. W. D. H.

Attempts to Produce Citric Acid from Alcohol and Lactose by Fungi. CARL WEHMER (*Chem. Zeit.*, 1913, **37**, 1393—1394. Compare Mazé and Perrier, A., 1904, ii, 676; Herzog and Polotzky, A., 1909, i, 285; Wehmer, this vol., i, 229).—Unsuccessful attempts are recorded to produce citric acid from alcohol or from lactose by means of fungi. The author thus confirms Herzog and Polotzky's conclusion with regard to the non-formation of citric acid from alcohol (contrast Mazé and Perrier), but differs from them in finding that it is also not produced from lactose.

Two species of *Citromyces* were grown during several months in a nutrient solution containing ammonium nitrate, potassium phosphate, magnesium sulphate, calcium carbonate, and alcohol (2·5 and 5%). The latter exerts a marked retarding effect on the growth of the fungi, which differs in extent for the two species. Citric acid could not be detected.

Under similar conditions, a like result was obtained with lactose solutions, in which, however, growth of the fungi occurred readily.

H. W.

Disinfectants which Dissolve Lipoids. JOSEF GÖSSL (*Zeitsch. physiol. Chem.*, 1913, **88**, 103—108).—Overton and Meyer pointed out that certain anæsthetics owe their activity to the fact that they are soluble in the cell-lipoids. A large number of chemical substances are examined in the present research to see if this also holds for their disinfecting powers, with the result that the answer is in the affirmative. The experiments were made on yeast cells.

W. D. H.

Nitrate and Nitrite Assimilation. OSKAR BAUDISCH (*Zeitsch. angew. Chem.*, 1913, **26**, 612—613. Compare A., 1911, ii, 523; 1912, ii, 286; this vol., i, 324).—Some new experiments in support of the view that nitroxyl, NOH, plays an important part in the assimilation of nitrogen have been carried out, partly on the heights of Monte Rosa, where the activity of the light was nearly equal to that of a mercury lamp. It was found that the liberation of oxygen from solutions of potassium nitrite or nitrate was greatly accelerated by carbon dioxide. Nitric oxide in presence of formaldehyde or methyl alcohol soon produced formhydroxamic acid. Nitric oxide and water, with yellow phosphorus as catalyst, gave ammonium nitrate in sunlight, and ammonium nitrite in mercury light. Nitric oxide itself was detected in moist air which had been passed through dilute alkali and then exposed to brilliant sunlight. Substances of the nature of α-amino-acids were obtained by the action of mercury light on potassium nitrite in presence of carbon dioxide, with ferric chloride as catalyst. A new course for the photo-synthesis of organic substances from air, carbon dioxide, and water is thus indicated. Ammonia was oxidised to nitrous acid in presence of oxygen under the influence of mercury light.

A diagram is given which summarises the numerous photo reactions between simple carbon, nitrogen, and oxygen compounds, which Baudisch, Piloty, and Stoklasa have already discovered.

J. C. W.

The Influence of Sodium Sulphate on the Growth of Plants. EMIL HASELHOFF (*Landw. Jahrb.*, 1913, **44**, 641—650).—An account of numerous culture experiments undertaken for the purpose of demonstrating the influence of sodium sulphate on the growth of *Vicia faba*, *Phaseolus vulgaris*, *Hordeum vulgare*, and *Zea mays*; the results are exhibited in tabular form.

F. M. G. M.

Uniformity of Structure of the Proteins. Their Changes in Vegetable and Animal Organisms. DMITRI N. PRIANISCHNIKOV (*Biol. Zentr.*, 1913, **42**, 679—682; from *J. exper. Landw.*, 1912).—Certain plants, such as barley, when supplied with ammonium chloride produce amides at the expense of proteins, whilst the ammonia is also converted into asparagine or glutamine. No accumulation of ammonium salt takes place. In the case of peas and vetches, ammonium salts do not increase the amount of asparagine, and may even diminish it. When, however, calcium carbonate is supplied along with an ammonium salt, the latter is converted into asparagine. With lupines, the presence of ammonium salts, both alone and with calcium carbonate, diminishes the amount of asparagine, whilst the plant accumulates ammonia, chiefly from cleavage products of the proteins.

Lower plants can accumulate ammonia without injurious effects. In lower animals proteins are degraded to ammonium salts, which are not completely converted into amides.

N. H. J. M.

Effect of Chloroform on the Respiratory Exchanges of Leaves. D. THODAY (*Ann. Bot.*, 1913, **27**, 697—717).—Different varieties of leaves, when treated with small amounts of chloroform, showed increased absorption of oxygen and a similarly increased production of carbon dioxide. In starved leaves the stimulation was generally prolonged.

When the amount of chloroform was sufficient to cause visible disorganisation, the production of carbon dioxide was diminished, whilst the absorption of oxygen was no longer closely correlated with the production of carbon dioxide.

Leaves of *Tropaeolum*, which contain no tannin, showed a depression of oxygen absorption greater than that of the production of carbon dioxide. In leaves of cherry, Portugal laurel, and *Helianthus*, which contain tannins, the absorption of oxygen was very rapid for a short time, and, although quickly falling, remained at a much higher level than the production of carbon dioxide.

N. H. J. M.

Methyl Alcohol of Leaves. MAURICE NICLOUX (*Bull. Soc. chim.*, 1913, [iv], **13**, 939—943).—The author has applied his method (this vol., ii, 1080) to distillates from various leaves, and has found the following quantities of methyl alcohol: ivy, 0·36 gram; spindle-tree (*Euonymus*), 0·45 gram, per kilo. of leaves. In the case of the ivy leaves, the calculations give a negative quantity for formaldehyde, due possibly to the presence of a small quantity of

ethyl alcohol or some similar substance which consumes potassium dichromate without yielding carbon dioxide. It is suggested that methyl alcohol may originate in plants in accordance with the equation $CO_2 + 2H_2O = CH_3{\cdot}OH + O_3$. Such an action would require a chlorophyll coefficient above 1, and thus be in harmony with Maquenne and Demoussy's observations (this vol., i, 232 and 429).

T. A. H.

Oxydases and their Inhibitors in Plant Tissues. WILLIAM R. G. ATKINS (*Sci. Proc. Roy. Dubl. Soc.*, 1913, **14**, 143—156. Compare Keeble and Armstrong, A., 1912, ii, 673; this vol., i, 325, 803).—The absence of a brown colour in the sap expressed from plant tissues may be due: (1) to the absence of organic peroxide; (2) to the presence of tannin, preventing the action of the oxydase; or (3) to the presence of some reducing agent or inhibitor. It is considered that oxydase is concerned in the production of cork and sclerenchyma. The distribution of oxydase and of a reducing agent in Iris species is described. The colours of Iris are due to the presence or absence of a yellow plastid pigment and an anthocyan pigment. A reducing substance active in aqueous solution may inhibit the production of anthocyan pigment.

E. F. A.

The Presence of a New Diastase, Salicinase, in Almonds. GABRIEL BERTRAND and ARTHUR COMPTON (*Compt. rend.*, 1913, 157, 797—799. Compare A., 1912, i, 592).—From a study of the temperature and the reaction of the medium, which, under definite conditions, favour the greatest activity of preparations of emulsin from almonds on salicin, the authors consider that their results point conclusively to the presence of a specific enzyme, *salicinase*, capable of hydrolysing salicin.

W. G.

Flower Pigments of Antirrhinum majus. II. Pale Yellow or Ivory Pigment. MURIEL WHELDALE and HAROLD LLEWELLYN BASSETT (*Biochem. J.*, 1913, 7, 441—444).—The pale yellow or ivory pigment present in each of the main classes of varieties of *Antirrhinum* with the exception of the white is identified as apigenin. In the plant it exists as a glucoside, and is present in the inner tissues.

E. F. A.

The Trypsin of Calotropis procera R.Br. and the Poison which Accompanies It. C. GERBER and P. FLOURENS (*Compt. rend.*, 1913, **157**, 600—603).—The latex of *Calotropis procera* contains a proteolytic enzyme, which is very resistant to heat, and more active in alkaline than in neutral medium. It coagulates milk, and digests casein and fibrin. Separated from the latex by the usual methods, it is eight to ten times less active than the latex itself, owing to its lability towards the agents used in the separation.

Its physiological action varies according to the animal used, and is due to a poison which accompanies it. Subcutaneously injected into a white rat, a rabbit or a fowl, it produces only a local effect

the skin and muscle, which disappears in a few days. In the case of the guinea-pig, pigeon, and certain cold-blooded animals, it is rapidly fatal. The deaths and premonitory symptoms are similar in character to those observed with the latex of *Broussonetia papyrifera*. The toxic substance can be extracted in the form of a brown solid, by maceration with alcohol. W. G.

Partial Decomposition of Yeast-nucleic Acid by the Press Juice of Cortinellus edodee. KWANJI TSUJI (*Zeitsch. physiol. Chem.*, 1913, **87**, 379—381).—The pressed juice of the fungus *Cortinellus edodes* produces guanosine from yeast-nucleic acid, indicating that it contains enzymes converting nucleic acid into nucleosides and hydrolysing the latter. E. F. A.

Capoc and Acon and their Bitter Constituents, Waxes, and Resins. HERMANN MATTHES and LOTHAR STREICHER (*Arch. Pharm.*, 1913, **251**, 438—452).—An examination of capoc and acon fibres. Java capoc, in contrast to cotton, contains cellulose 64·3%, lignin 13%, and pentosans 23—24%. Capoc and acon fibres are brittle, and contain 8·6% and 7·2% respectively of moisture, and about 7—10% of constituents soluble in water. Acon wax (4·63%), m. p. 39·5°, n_D^{40} 1·4682, acid number 65·09, ester number 106·43, saponification number 171·52, iodine number 70·52, Reichert-Meissl value 1·76, Polenske value 1·05, contains about 31% of unsaponifiable constituents, consisting of melicyl alcohol, a *hydrocarbon*, $C_{20}H_{42}$, m. p. 69° (probably laurane), and liquid and solid phytosterols; from the latter, a *phytosterol*, m. p. 136°, and another, m. p. 170° (probably stigmasterol), have been isolated. The fatty acids obtained from acon wax consist of about 20% of solid, and about 80% of liquid, acids. The solid acid consists only of palmitic acid; the liquid acids contain about 61% of oleic acid, 38% of linolic acid, and 1% of linolenic acid.

Capoc wax, m. p. 24°, n_D^{40} 1·4618, acid number 59·85, ester number 110·29, saponification number 170·14, iodine number 69·44, Reichert-Meissl value 2·02, Polenske value 0·97, contains about 28% of unsaponifiable constituents, and yields about 15% of palmitic acid, and 85% of liquid acids similar to those obtained from acon wax.

Capoc and acon possess a bitter taste. This is due to a substance which has been isolated from acon. It is a yellow substance, which is strongly poisonous, dissolves in water, reduces ammoniacal silver oxide and Fehling's solutions, develops with sulphuric acid and potassium dichromate a blue colour changing to green, and gives precipitates with the alkaloidal reagents, although it does not contain nitrogen. It resembles picrotoxin in being decomposed by boiling chloroform into a soluble and an insoluble component.

Acon fibres contain chlorophyll and a resin. C. S.

The Existence of a Cyanogenetic Compound in a Member of the Papaveraceæ (Papaver nudicaule). MARCEL MIRANDE (*Compt. rend.*, 1913, **157**, 727—729).—The author has examined the

leaves of plants of *Papaver alpinum*, of hybrids between this and *P. nudicaule*, and of nearly pure *P. nudicaule* for a cyanogenetic compound. The aqueous distillate of the leaves contains hydrocyanic acid in the case of the hybrids and *P. nudicaule*, but none in the case of *P. alpinum*. The plants with yellow flowers contain more of this compound than those with red or white flowers, and the nearer the plant is to the pure type, *P. nudicaule*, the higher is the yield of hydrogen cyanide. This is the first instance of a member of the Papaveraceæ containing a cyanogenetic compound. W. G.

Robin and the "Phasin" of Robinia Seeds. ROBERT KOBERT (*Landw. Versuchs.-Stat.*, 1913, **79-80**, 176—181. Compare succeeding abstract).—The name "robin" was applied by Kobert to a protein first prepared from the bark of *Robinia pseudacacia* by Power in 1889 (*Pharm. Rundschau*, 1890, **8**, 29), and subsequently characterised more completely by the same author (A., 1901, ii, 679), who showed especially (1) that it was toxic, but lost its poisonous properties when heated; (2) that it hydrolysed amygdalin and sinigrin; and (3) coagulated milk like rennet ferment. These observations, especially as regards the physiological action of the substance, were confirmed and extended by Lau (*Diss.*, Rostock, 1906 (?1901)), Ehrlich (*Klin. Jahrb.*, 1898, **6**, 315), and others, including the present author. In the present paper it is shown: (1) that "robin" undoubtedly behaves as a agglutinant with blood of various kinds; (2) is not toxic when injected subcutaneously into rabbits in quantities of 1 to 10 c.c. of a 4% solution; (3) does not hydrolyse sinigrin; (4) does not coagulate milk; and (5) does not precipitate ricin-serum. The toxicity of the "robin" preparations examined by Lau is ascribed to impurity or to the use of abnormally large doses of the material. The toxicity of the bark, it is suggested, may be due to the alkaloid or the glucoside it contains. From Robinia seeds a similar "phasin," which agglutinates blood, but is not toxic and has no glucosidolytic activity, has been prepared. T. A. H.

Poisonous Constituent of the Bark of Robinia pseudacacia. FREDERICK B. POWER (*Amer. J. Pharm.*, 1913, **85**, 339—344. Compare *Pharm. Rundschau*, 1890, **8**, 29; A., 1901, ii, 679).—The author traverses the statements made by Kobert (preceding abstract) as regards the toxicity, glucosidolytic activity, and milk-clotting property of "robin." Repetition of some of his previous experiments with a sample of "robin" prepared in 1904 shows that the material is still poisonous, and is capable of hydrolysing sinigrin and amygdalin. T. A. H.

Hydrogen Cyanide in Salt-Grass (Triglochin). JAN J. BLANKSMA (*Pharm. Weekblad*, 1913, **50**, 1295—1302. Compare Greshoff, *ibid.*, 1908, **45**, 1167).—Greshoff's observation of the occurrence of hydrogen cyanide in salt-grasses is confirmed. The proportion is highest in the flowers and young fruit, and falls off as the fruit ripens. These grasses contain no acetone, but

maceration with water produces ethyl alcohol and acetaldehyde, even from varieties not containing hydrogen cyanide. The mode of combination of the hydrogen cyanide in the grasses is a matter of doubt. A. J. W.

The Presence of a Nitrogenous Substance in the Seedlings from Vicia Faba. TORQUATO TORQUATI (*Chem. Zentr.*, 1913, ii, 517—518; from *Arch. Farm. sperim.*, 1913, **15**, 213—223).—A substance of the approximate formula $C_{11}H_{15}O_5N$, m. p. 273—275°, was isolated from the seedlings in the following way. The disintegrated material was extracted with hot water acidified with acetic acid. The proteins and pectins were separated from the filtrate by lead acetate. The filtrate from these, on neutralisation with ammonia, yielded a light yellow precipitate. This was decomposed with hydrogen sulphide, and a substance precipitated from the solution thus obtained by basic lead acetate. On decomposing the precipitate thus formed by hydrogen sulphide and concentration of the solution, the above-mentioned substance separated in crystalline form. The substance is neutral and rapidly darkens, especially in the presence of alkalis. With potassium ferrocyanide and ammonia it yields a ruby-red solution, which rapidly darkens. Permanganate is quickly reduced by it in acid solution, and it also reduces various mercuric, silver, and copper salts. S. B. S.

The Presence of a Nitrogenous Substance in the Green Pods of Vicia faba. TORQUATO TORQUATI (*Chem. Zentr.*, 1913, ii, 518; from *Arch. Farm. sperim.*, 1913, **15**, 308—312).—In addition to tyrosine, discovered by Bourquelot and Hérissey, the author has succeeded in obtaining the same chromogenic substance as that got by him from the seedlings (see preceding abstract). This substance is not contained in the seeds themselves nor in the pods of *Pisum*. S. B. S.

Calcareous Chlorosis of Green Plants. Rôle of the Root Excretions in the Absorption of Iron from Calcareous Soils. PIERRE MAZÉ, M. RUOT, and M. LEMOIGNE (*Compt. rend.*, 1913, **157**, 495—498. Compare A., 1912, ii, 1088).—The chlorosis, which is induced in plants grown in water cultures containing an excess of calcium carbonate in suspension or soluble calcium salts in solution, can be destroyed by the addition of small quantities of organic acid to the culture solutions, the green colour returning to the leaf. The appearance of chlorosis is accompanied by a pink coloration of the culture liquid, and this gradually disappears after the addition of the acid. W. G.

[The Lime-Magnesia Ratio.] JOHN A. VOELCKER (*J. Roy. Agric. Soc.*, 1912, **73**, 325—338).—Wheat was found to be benefited by the addition of magnesia to soil in which magnesia is deficient, provided that the magnesia does not exceed the lime. An excess of magnesia over lime has a toxic effect, and diminishes the yield. Addition of lime will then be beneficial, and an excess of lime does not possess the toxic effect which magnesia in excess has.

Both magnesia and lime are capable of modifying the growth of wheat, and altering the character of the root and the composition of the grain. N. H. J. M.

Influence of Lithium, Zinc and Lead Salts on Wheat. JOHN A. VOELCKER (*J. Roy. Agric. Soc.*, 1912, **73**, 314—325. Compare A., 1911, ii, 922).—The results of pot experiments showed that lithium salts are toxic when the soil contains 0·003% or more of lithium, whilst amounts not exceeding 0·002% have a stimulating effect. The best results are obtained with the nitrate (which is the most stimulating, as well as the most toxic of the different salts) when the amount of lithium does not exceed 0·001%.

Zinc salts have a slightly stimulating action on wheat when the soil contains less than 0·02% of zinc. Larger amounts of zinc have a toxic action.

Lead salts have no toxic effect when the soil contains as much as 0·03% of lead. The nitrate seems to have a stimulating effect.

It is worthy of note that much larger amounts of zinc than of lithium may be present in the soil without having any injurious action on wheat, the relative amounts being 10 : 1.

As regards the period in which the stimulating action takes place, the results so far obtained seem to indicate that it is during the germination of the seed rather than later. The action may result in considerable alterations in the development of the plant, in root production, and even in the character of the grain. N. H. J. M.

The Conditions which Affect the Activity of the Amylolytic Enzymes in Wheat Flour. C. O. SWANSON and JOHN W. CALVIN (*J. Amer. Chem. Soc*, 1913, **35**, 1635—1643).—It is known that flour when mixed with water and allowed to digest for four hours at 60° shows great diastasic activity. The results of this investigation show that the optimum temperature for the production of the maximum amount of reducing sugars is near 65°, and that the best proportions of flour and water lie between 1 : 4 and 1 : 10, little difference being observable between these limits. The transformation is mainly effected in the first hour (approx. 88% of the total change), and under favourable conditions more than two-fifths of the flour undergoes conversion into soluble substances (calculated as maltose). Small quantities of sulphuric acid, sodium hydroxide, dipotassium hydrogen phosphate, and sodium chloride all exert an inhibitory effect on the action of the enzymes of the flour, the influence being most marked with sodium hydroxide, and least with sodium chloride. Although little difference is observable between the quantities of reducing sugars formed in the action of water on various grades of flour from the same wheat, the inhibitory effect of the chemicals named is less marked with a low grade than with a straight flour. D. F. T.

The Amounts of Sulphur and Chlorine in the Rice Plant. ALICE R. THOMPSON (*J. Amer. Chem. Soc.*, 1913, **35**, 1628—1634).—An investigation on the effect of fertilisers on the sulphur and

the rice content of the plant grown in natural soil conditions and in sand cultures. The plant was analysed before flowering, the foliage and roots being examined separately; a second examination was made of the panicles, leaves, stems, and roots at the flowering period, and a third was made of the chaff, grain, leaves, stems, and roots at maturity. Analysis was also made of the soil of the rice fields and of the water supplied.

The results of the analyses are tabulated in the original.

D. F. T.

Relationship between the Weight of the Sugar Beet and the Composition of its Juice. J. ARTHUR HARRIS and ROSS A. GORTNER (*Biochem. Bull.*, 1913, **2**, 524—529).—The wide-spread belief that largo beets contain less sugar % than small beets is shown to rest upon very slender foundations. W. D. H.

The Influence of Growth in the Shade on the Various Constituents of Tobacco. ALBERT STUTZER and SAMUEL GOY (*Biochem. Zeitsch.*, 1913, **56**, 220—229).—Comparisons were made of the nicotine and potassium contents of the leaves from plants which were grown in pots in the shade, and from those grown under similar conditions in direct sunlight. There was less organic matter in those grown in the shade, but the percentages of nitrogen were higher. Both series of plants were richly fed with urea nitrate. In the lower leaves from the shaded plants the amount of nicotine was both absolutely and relatively higher than in the leaves of the other plant. In the upper leaves, however, the relative percentage of nitrogen in the form of nicotine in the shaded plants was less than that in the unshaded. The dried material of the shaded plants contained more potassium than that of the unshaded.

S. B. S.

Lævulose in the Leaves of Kentucky Tobacco Grown in Italy. FILIPPO TRAETTA-MOSCA (*Gazzetta*, 1913, **43**, ii, 428—430).—By analysis of the leaves of this tobacco, the author has isolated a sugar which was identified as lævulose by means of its phenylglucosazone, rotatory power, and other properties. R. V. S.

The Ferments of Plants of Kentucky Tobacco Grown in Italy. FILIPPO TRAETTA-MOSCA (*Gazzetta*, 1913, **43**, ii, 431—437).—A glycerol extract of the green leaves of this tobacco appears to contain oxydases, peroxydases, catalases, invertase, amylases, lipases, emulsin, and proteolytic ferments. R. V. S.

Titanium and Rare Metals in the Ashes of Leaves of Kentucky Tobacco Grown in Italy. FILIPPO TRAETTA-MOSCA (*Gazzetta*, 1913, **43**, ii, 437—440).—In the leaves of this tobacco, the author has detected lithium, cæsium (both spectroscopically), titanium (spectroscopically and by colour reactions), and barium, as well as the other elements previously found in this plant.

R. V. S.

The Ethereal Extract of the Leaves of Kentucky Tobacco Grown in Italy. FILIPPO TRAETTA-MOSCA (*Gazzetta*, 1913, **43**, 440—445).—That portion of the substances extracted with ether which is insoluble in cold alcohol yields a white *substance*, m. p. 62—63°, which gives the Liebermann-Burchard reaction for ethers of the sterols, and contains 8·54% of oxygen (compare Thorpe and Holmes, T., 1901, **79**, 982). The resin of the leaves is a substance of high molecular weight (690), which yields a bromo-derivative, m. p. 118° (decomp.), and contains 61·59% of bromine but no oxygen. Oxidation of the resin with nitric acid yields a *substance*, $C_8H_{12}O_4$, m. p. 55—56°, possibly a hexahydrophthalic acid. Its *ammonium* salt yields colloidal solutions of a very typical character. R. V. S.

First Results of Manuring Vines with Manganese Sulphate. F. A. SANNINO and A. TOSATTI (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 237—242).—In one year's experiment the yield was considerably increased (possibly owing to the added sulphate), but the dextrose of the product was less than in the case of the unmanured vines, and the acidity was greater. In the second year the increase in yield was not so marked, and the dextrose and acid were present in about normal amounts. Details are given of the testing of the wines made from the manured and from the unmanured vines.

R. V. S.

Typical Peats. HERMANN MINSSEN (*Landw. Jahrb.*, 1913, **44**, 269—330).—A comprehensive study of different kinds of peat obtained from many localities, by which the author attempts to draw up a classification. Two great groups of peat formation are indicated, that is, the peats of "high" bogs and those in "low" positions, and between these many minor types exist. The different plants of which peats are formed are studied, and the results of numerous analyses tabulated, with a discussion on the possible significance of the facts observed. F. M. G. M.

Manurial Experiments with Calcium Cyanamide, Sodium Nitrate, and Ammonium Sulphate on Sand and Peat Soils. BRUNO TACKE and FR. BRÜNE (*Landw. Versuchs.-Stat.*, 1913, **83**, 1—100).—Frank's calcium cyanamide and Polzeniuss's calcium cyanamide (which contains calcium chloride) give similar results on sandy soils. On peaty soil the latter only had 81% of the value of Frank's manure.

Calcium cyanamide should be applied not with the seed, but at least a week beforehand; and it should at once be harrowed in. Different crops show different degrees of sensitiveness, rye being more sensitive than oats and potatoes when the manure is applied as top dressing, whilst oats is specially liable to injury when the manure is applied at the same time as the seed. As regards the utilisation of nitrogen, calcium cyanamide was far behind ammonium sulphate and sodium nitrate. N. H. J. M.

General and Physical Chemistry.

Leisegang's Rings and Related Phenomena. ERNST KÜSTER (*Kolloid. Zeitsch.*, 1913, **13**, 192—194).—The iridescence which makes its appearance when a solution containing alkali metal phosphates and alkali hydroxide is allowed to diffuse into a gelatin jelly containing calcium chloride is shown to be due to the folding of a delicate membrane which is formed at the surface of the gelatin. The original explanation of the phenomenon (Liesegang, this vol., ii. 453) attributed the iridescence to the formation of concentric layers of precipitate, but various observations are described which indicate that this view is untenable.

It is also shown that a periodic variation of the external conditions may lead to the formation of differentiated zonal regions in colloidal systems. H. M. D.

An Oxidisable Variety of Nitrogen. T. MARTIN LOWRY (*Trans. Faraday Soc.*, 1913, **9**, 189—192. Compare T., 1912, **101**, 1152).—Photographs of spectra illustrating the conclusions already published. C. H. D.

Emission and Absorption of Heated Carbon Dioxide. HANS SCHMIDT (*Ann. Physik*, 1913, [iv], **42**, 415—459).—The absorption and emission of layers of carbon dioxide have been determined for a number of temperatures (435—900°) and wave-lengths. With homogeneous heating carbon dioxide gives rise to the emission and absorption band spectrum which was discovered by Paschen. This points to the fact that gases can be made to emit a discontinuous spectrum by raising their temperature. At constant pressure the absorption bands increase on the long wave-length side as the temperature is increased. It is shown that in all probability the Kirchhoff law holds quantitatively for homogeneously heated carbon dioxide. J. F. S.

The Influence of Concentration and of Different Colourless Metal Ions on the [Light] Absorption of Coloured Salt Solutions. ARTHUR HANTZSCH and, in part, C. S. GARRETT and F. GAJEVSKI (*Zeitsch. physikal. Chem.*, 1913, **84**, 321—347).—The absorption spectra and extinction coefficients of aqueous and alcohol solutions of the alkali and alkaline earth salts of chromic acid, hydroferrocyanic acid, chloroplatinic acid, and those of methyloxindone, acetyloxindone, and oxindonecarboxylic ester have been determined. Whilst in the experiments it is shown that the ions of coloured salts are optically identical, or nearly so, with the undissociated salt, still the different solvents exercise an optical effect on the coloured ions. This effect is more marked the less saturated the components are, which may be explained by the formation of solvates. Small divergences from Beer's law are only to be found

in very concentrated alkaline solutions of chromates and possibly ferrocyanides by the extinction method. These divergences are probably to be explained by incomplete hydration rather than by dissociation changes. It is shown that the analogous observations of Jones (A., 1912, ii, 507, 216) for concentrated solutions, and Baly (T., 1913, **101**, 91) for pyridine solutions, are probably not physical changes, but chemical, and due to a shifting of the equilibrium point of different complex ions, or perhaps hydrates. This result is confirmed by the following. All variations of the colorimetric dilution law are due either to experimental errors or to chemical changes of the substances by the solvent. The absorption of saturated and constitutionally unchangeable inorganic coloured anions is so slightly changed by the different cations that the influence of the cation could only be detected by the extinction method. The absorption of unsaturated coloured organic anions of unchangeable structure is only changed by the different cations at the highest concentrations, and then only in non-aqueous solutions; this is brought about by the auxiliary valencies of cations combining with the residual valencies of the anions. The absorption of the coloured alkali and alkaline earth organic salts decreases with the decreasing positive character of the cation, the order being: Cs–Rb–K–Na–Li–Ba–Sr–Ca. The optical effects observed here are relatively small when compared with the changes which the same metals bring about in solutions of polychromatic acids through structural alterations of the anions. As a general result it is shown that the changes in light absorption of coloured substances correspond with constitutional changes, or, in other words, the absorption changes more the more the constitution changes. J. F. S.

The Dependence of the Light Absorption of Some Metallic Salts on the Nature of the Linking. I. Mercuric Salts. HEINRICH LEY and W. FISCHER (*Zeitsch. anorg. Chem.*, 1913, 82, 329—340).—The ultra-violet absorption of mercuric salts is displaced towards longer wave-lengths in passing from the chloride to the iodide, the bromide being exactly intermediate. The iodide has an absorption band. The undissociated salt in alcoholic solution may be compared with its component ions by using mercuric perchlorate, which is highly dissociated, in a tube placed in series with one containing a solution of the corresponding potassium salt. In this way it is found that salt formation is accompanied by a bathochromic effect, which is greatest in the iodide. Mercuric cyanide is almost as diactinic as water, and much more so than mercuric ions, a result which is explained by the presence of a mercury–carbon linking. In accordance with this, mercury methyl chloride and mercury ethyl chloride absorb less than mercuric chloride. On the other hand, compounds with mercury linked to nitrogen, such as mercury propionamide and mercury succinimide, have a high absorption.

Mercurous perchlorate absorbs more than the mercuric salt,

favouring the view that a bivalent complex ion $(Hg\cdot Hg)^{\cdot\cdot}$ is present.
C. H. D.

Quantitative Investigation of the Absorption of Ultra-violet Rays by Saturated and Unsaturated Aliphatic Acids. III. JAN BIELECKI and VICTOR HENRI (*Ber.*, 1913, **46**, 2596—2607. Compare this vol., ii, 263).—The authors have extended their studies from monobasic fatty acids to polybasic saturated and unsaturated acids and their corresponding hydroxy-acids. The molecular coefficients of absorption for different wave-lengths are tabulated, and curves are also given. The results are summarised as follows:

(1) In the case of saturated acids (acetic, oxalic, malonic, succinic, and tricarballylic) a considerable exaltation of the absorption is caused by increasing the number of carboxyl groups, and the exaltation rises faster than the number of these groups.

(2) Saturated acids have about the same absorption as their corresponding hydroxy-acids (propionic and α-hydroxypropionic acids, succinic, malic, *d*-tartaric and racemic acids, tricarballylic and citric acids), but the small exaltation caused by the alcoholic hydroxyl group is much greater than the absorption of the corresponding normal alcohol.

(3) Ethylenic acids (allylacetic, itaconic, α-crotonic, fumaric, maleic, mesaconic, citraconic, and aconitic acids) are much more absorbent than the saturated acids, and the exaltation effect of the double linking is much stronger the nearer it is to the carboxyl group (compare Macbeth, Stewart, and Wright, T., 1912, **101**, 603). The exaltation is much greater in the case of corresponding saturated and ethylenic acids than in the case of corresponding alcohols.

(4) The acetylenic linking (methyl propiolate and ethyl acetylenedicarboxylate) has not such a great influence as the ethylenic linking, but the position of the triple bond with respect to the carboxyl group is of the same importance.

(5) Stereoisomeric acids have different absorptive powers, and *trans*-isomerides show higher values than the *cis*-forms.

(6) As was previously found (*loc. cit.*), the acids are more absorbent in alcohol than in water, with the exception of maleic acid, in which case the converse is true.

(7) Aconitic acid, having three carboxyl groups and a double linking between two carbon atoms, each of which bears a carboxyl group, has an enormous absorption constant, the highest of all the acids studied.

As a general result of their studies in this field the authors come to the conclusion that the effect of different chromophores in a molecule is not additive, but that the absorption constant is equal to the product of the "absorption factors," corresponding with the several chromophores, and the "exaltation factors," which depend on the relative position of the chromophores in the molecule. These factors have different values for different wave-lengths, and appear to be complicated functions of the frequency.
J. C. W.

The Absorption Spectra of White and Yellow Santonin. ARNALDO PIUTTI (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 192—204). —Carbon electrodes which have been alternately heated to redness and immersed in ferric chloride solution a few times, or a carbon and an iron electrode, may be employed with advantage instead of iron electrodes for the arc used as a source of light in these experiments. The curves obtained indicate that the transformation of santonin into photosantonic acid and *iso*photosantonic acid by light proceeds by way of intermediate compounds. Photosantonic acid, and probably also *iso*photosantonic acid, are very transparent to the ultraviolet rays, but santonin is not. No confirmation could be obtained of the alleged re-conversion of yellow santonin into white on boiling. The alleged visible alteration of santonin crystals under the action of light could not be observed.

Asparagine, lactic acid, and carbamide are almost completely transparent to the light of the iron arc. R. V. S.

The Absorption of the Visible and Ultra-violet Rays by the Carotinoid Pigments. CHARLES DHÉRÉ and L. RYNCKI (*Compt. rend.*, 1913, **157**, 501—504. Compare A., 1912, i, 867).—A study of the absorption spectra in the visible and ultraviolet portion of the spectrum of the two pigments, carotine and xanthophyll. Photographs are given of these spectra for the first-named pigment. They exhibit a relatively considerable transparency for all the ultraviolet radiations up to $\lambda = 225\,\mu\mu$. W. G.

The Absorption of the Visible Rays by the Oxyhæmocyanins. CHARLES DHÉRÉ and A. BURDEL (*Compt. rend.*, 1913, 157, 552—555).—A study of the absorption spectra of oxyhæmocyanins from various sources, in solution in sodium chloride ($N/5$) and sodium carbonate ($N/100$). Reproductions are given of three spectrophotographs, and the results seem to show that there is an absorption band common to all the oxyhæmocyanins. On reducing these substances to hæmocyanins, the band disappears, but is restored by agitating the solution with air. W. G.

Connexion Between Fluorescence and Ionisation. MAX VOLMER (*Ann. Physik*, 1913, [iv], **42**, 485—486).—Polemical. A reply to Stark's criticism (this vol., ii, 743) of the author's paper (this vol., ii, 456). J. F. S.

Connexion Between Fluorescence and Ionisation. WILHELM E. PAULI (*Ann. Physik*, 1913, [iv], **42**, 487).—Polemical. A reply to Stark's criticism (this vol., ii, 743) of the author's paper (this vol., ii, 456). J. F. S.

A Silica-jacketed Silica Polarimeter Tube. T. MARTIN LOWRY (*Trans. Faraday Soc.*, 1913, **9**, 193).—The silica jacket is fused on to the silica tube, with a fused joint where the central tube passes through the jacket. The metal ends are slotted to receive the silica water tubes, and are cemented on. C. H. D.

Investigation of Nitro celluloses in the Polarisation Microscope. HANS AMBRONN (*Kolloid. Zeitsch.*, 1913, **13**, 200—207).—From an examination of a series of nitrocelluloses by means of the polarisation microscope, the author has found that there is a definite connexion between the nitrogen content of the substance and the optical properties of the fibres. When the percentage of nitrogen is small, the double refraction is positive. As the nitrogen content increases, the refractive power falls to zero, and in the case of the more highly nitrated products the double refraction is negative, becoming more and more negative as the percentage of nitrogen increases. The change in the character of the double refraction appears to vary continuously with the nitrogen content.

Similar changes in the optical properties have been found in the case of nitrated ramie fibre, and for this material it has been observed that the denitrification of the fibre by treatment with ammonium sulphide yields a product which in regard to its optical properties is identical with the original ramie fibre previous to nitrification.

It is suggested that the polarisation microscope may find useful application in the nitro-cellulose industry, and in particular that it may be employed in the estimation of the nitrogen content.

H. M. D.

Optical Superposition. LEO TSCHUGAEV and A. GLEBKO (*Ber.*, 1913, **46**, 2752—2762).—The *l*-menthylurethane of ethyl *d*-tartrate has $[\alpha]_C$ $-58\cdot31°$, $[\alpha]_D$ $-74\cdot34°$, $[\alpha]_E$ $-96\cdot77°$, and $[\alpha]_F$ $-119\cdot97°$ at 22° in acetone ($c=7\cdot80$). The *l*-menthylurethane of ethyl *l*-tartrate has $[\alpha]_C$ $-31\cdot04°$, $[\alpha]_D$ $-38\cdot76°$, $[\alpha]_E$ $-48\cdot64°$, and $[\alpha]_F$ $-57\cdot44°$ under similar conditions ($c=6\cdot48$). The *l*-menthylurethane of ethyl mesotartrate has $[\alpha]_C$ $-45\cdot14°$, $[\alpha]_D$ $-57\cdot78°$, $[\alpha]_E$ $-74\cdot16°$, and $[\alpha]_F$ $-89\cdot77°$ ($c=7\cdot75$), values which are within 2% of those calculated by van't Hoff's principle of optical superposition. The *dl*-fenchylurethane of ethyl *d*-tartrate has $[\alpha]_C$ $-27\cdot41°$ ($-35\cdot59°$), $[\alpha]_D$ $-35\cdot29°$ ($-45\cdot40°$), $[\alpha]_E$ $-46\cdot76°$ ($-59\cdot47°$), and $[\alpha]_F$ $-58\cdot58°$ ($-74\cdot01°$) at 21° in acetone ($c=5\cdot58$) and chloroform ($c=4\cdot23$), the rotatory powers in brackets being those in the latter solvent. The *dl*-fenchylurethane of ethyl *l*-tartrate has $[\alpha]_C$ $+5\cdot82°$ ($1\cdot03°$), $[\alpha]_D$ $+7\cdot80°$ ($1\cdot91°$), $[\alpha]_E$ $11\cdot25°$ ($3\cdot53°$), and $[\alpha]_F$ $+13\cdot52°$ ($5\cdot59°$) in acetone ($c=4\cdot809$) and chloroform ($c=3\cdot397$) at 21°. The *dl*-fenchylurethane of ethyl mesotartrate has $[\alpha]_C$ $-11\cdot24°$ ($-16\cdot51°$), $[\alpha]_D$ $-14\cdot35°$ ($-20\cdot63°$), $[\alpha]_E$ $-18\cdot80°$ ($-26\cdot41°$), and $[\alpha]_F$ $-23\cdot07°$ ($-32\cdot74°$) in acetone ($c=5\cdot159$) and chloroform ($c=3\cdot64$) at 21°; these values are within 6% of those calculated by the principle of optical superposition. The authors assert, therefore, that the principle is tenable, at least as a first approximation (compare Patterson, T., 1905, **87**, 40; 1906, **89**, 1884; 1907, **91**, 705). The calculated values of the rotation dispersion-coefficients, $[\alpha]_F/[\alpha]_C$, of the two urethanes of the mesotartrate agree exactly with those actually observed. The results also show that the abnormally high values of the dispersion-coefficients of the fenchylurethane of ethyl *l*-tartrate are caused by

the superposition of the individual optical effects, thus confirming the view previously expressed (A., 1911, ii, 787) that a relation exists between abnormal rotation dispersion and optical superposition of the partial rotations corresponding with the individual centres of optical activity. C. S.

Spectral Distribution of Light Sensitiveness in Photochemical Reactions. JOH. PLOTNIKOV (*Zeitsch. Elektrochem.*, 1913, **19**, 753—754).—Polemical against Bruner (this vol., ii, 745). It is shown that that author's assertion, which states there is no evidence to show that photochemical reactions are influenced by the wave-length of the exciting light, is not in accord with facts (compare Plotnikov, A., 1911, ii, 4, 452). J. F. S.

Experimental Confirmation of Faraday's Law in Gas Reactions. SAMUEL C. LIND (*Zeitsch. physikal. Chem.*, 1913, 84, 759—761).—The author points out that Jellinek, in his treatise, "Physikalischen Chemie der homogenen und heterogenen Gasreaktionen," has entirely omitted the case of chemical reactions brought about by radioactive α-rays. These reactions, both from point of priority and from the manner in which they confirm Faraday's law, are equally, if not more, important than the reactions of Krüger and Möller (A., 1912, ii, 1126), which are included. The author cites a number of such reactions which have been studied quantitatively. J. F. S.

Scattering of α-Particles by Gases. ERNEST RUTHERFORD and J. M. NUTTALL (*Phil. Mag.*, 1913, [vi]. 702—712).—The scattering of α-particles in gases was investigated by causing α-rays of radium-C, from a fine platinum wire coated with the radium active deposit. to pass between two parallel plates of glass kept at various distances apart by mica strips, in a cylindrical chamber which could be filled with the gas under investigation at any pressure desired, and provided with a thin mica window at the other end for the escape of the α-rays into an ionisation chamber. Corrections for the decrease of ionisation due to loss of range of the α-particle in the gas were carried out directly in the same apparatus with the parallel plates removed. Over a certain range of pressure the loss of ionisation due to scattering, when gas at increasing pressure was admitted into the chamber, showed that the unscattered radiation varied exponentially with the pressure of the gas. For different distances between the plates, the scattering varied approximately as the 5/4th inverse power of the distance. The scattering coefficient was found to vary inversely as the fourth power of the velocity, and this, combined with the result that the scattering varies inversely as the pressure of the gas, shows that the effect is mainly due to single rather than compound scattering. The relative scattering per atom of hydrogen, helium, carbon, nitrogen, oxygen, and sulphur are respectively 0·0176, 0·064, 0·40, 0·48, 0·53, and 1·61, which agree, considering the difficulties of the experiment and the probable divergence between experiment and theory, for

the heavier atoms with the calculated numbers 0·0190, 0·057, *0·40*, 0·53, 0·69, and 2·58. The latter are derived from a formula deduced by Darwin, $\lambda = cn(n+1)$, where λ is the scattering coefficient, c a constant, and n the number of positive charges on the atomic nucleus (1, 2, 6, 7, 8, and 16 respectively for the above atoms). The results confirm the view put forward previously that the atom consists of a positively charged nucleus of small dimensions carrying a number of atomic charges equal to half the atomic weight and surrounded by a compensating distribution of negative charges. F. S.

Range and Ionisation of the Alpha Particle in Simple Gases. THOMAS S. TAYLOR (*Phil. Mag.*, 1913, [vi], **26**, 402—410).—The ranges found for the α-particles of polonium and radium-*C* are shown in the following table:

Range in cm. at 760 mm.

	0°		15°.		
	Po.	Ra-*C*.	Po.	Ra-*C*.	Ratio of ranges.
Air	3·57	6·57	3·77	6·93	1·84
Oxygen ...	3·25	5·94	3·43	6·26	1·83
Hydrogen.	15·95	29·36	16·83	30·93	1·84
Helium ...	16·70	30·84	17·62	32·54	1·84

The diminution in the number of α-particles towards the end of the range was found to be relatively more abrupt in air and oxygen than in hydrogen and helium, which is as is to be expected on the view that the heavier the atom through which the α-particle passes the greater the angle through which the particle is liable to be deflected. Ionisation-range curves were taken in helium, hydrogen, and air adjusted in pressure, so that the range in each was the same. The curves were very similar in shape, the area of the helium curve being 5% greater than that of the hydrogen curve, showing that the energy required to ionise a hydrogen atom is 5% greater than that for a helium atom. Geiger's formula (A., 1910, ii, 473) expressed the results well. F. S.

β-Rays of the Radium Family. JEAN DANYSZ (*Ann. Chim. Phys.*, 1913, [viii], **30**, 241—320).—A résumé of work on this subject is given, together with a detailed account of the author's own work already recorded in A., 1911, ii, 840; 1912, ii, 113, 219, 220, 617, 888; 1913, ii, 270. T. A. H.

Analysis of the β-Rays from Radium-*B* and Radium-*C*. ERNEST RUTHERFORD and H. ROBINSON (*Phil. Mag.*, 1913, [vi], **26**, 717—729).—A new method is described for photographing the spectrum of β-rays in a uniform magnetic field. The source of rays (thin-walled tube of emanation, wires coated with radium-*B* + -*C* or -*C* alone) is placed below a slit, and at the side of a lead block on which the plate is laid face upward, the slit being in the plane of the plate, and source, and parallel to the magnetic

field, which must be very uniform. The β-rays are coiled into circles, and strike the plate at different distances from the slit. A comparatively wide slit is used. All rays of the same radius of curvature which pass through even a wide slit intersect in the neighbourhood of the photographic plate, and thus leaving a quite sharp trace. Tables are given of the value of $H\rho$, the velocity β and energy E, calculated from $H\rho$ by the Lorentz-Einstein formulæ, for 16 lines due to radium-B and 48 lines due to radium-C, but more than 50 lines have been observed from the latter, the intensity of the different lines varying greatly. A plate is given showing diagrammatically the distribution of the lines along scales of $H\rho$ and E, and their relative intensity. For radium-B, no lines were observed with $H\rho$ above 2450 ($\beta = 0{\cdot}823$ in terms of the velocity of light). For radium-C the highest velocity lines which showed clearly had $H\rho = 8530$ ($\beta = 0{\cdot}9808$), but five faster lines are recorded (up to $H\rho = 9965$, $\beta = 0{\cdot}9858$), and a number still higher could be faintly seen. The lower limit of the complete record is $H\rho = 4840$, but below this the plates are crowded with fine lines, and only a few have been as yet included. These extend right into the low velocity regions where the radium-B lines are found. The rays of radium-C appear to be very closely homogeneous, the lines being sharp without indication of any widening. The energy of the various lines of radium-C appear to be integral multiples of $0{\cdot}4284 \times 10^{13}e$. For the higher groups the average difference is twice this, but between the multiples 24 and 44 all twenty are represented, and no lines are missing. The suggestion is made that the groups of β-rays observed are not due to the original β-particle expelled, which causes the disturbance, but to the emission of β-rays consequent on vibrations of definite systems of electrons within the atom. Below the multiple 24, the difference between the energies of successive lines is much smaller than that given, and the theoretical analysis of these slow velocity electrons presents great difficulties. F. S.

Scattering and Absorption of γ-Rays of Radium. J. A. GRAY (*Phil. Mag.*, 1913, [vi], **26**, 611—623).—The effect of placing radiators of different materials (carbon, iron, lead) to make different angles with a source of radium and an electroscope, screened from the direct γ-radiation, has been studied. The quantity of radiation scattered per unit mass is approximately independent of the nature of the radiator. The reason why lead appears to give much less scattered radiation than carbon and iron, which give about the same, is due to the relatively greater absorption of the scattered radiation in the lead. The quality of the scattered radiation depends on the angle of scattering, and not on the radiator, being the softer the greater the angle. The softer the primary γ-rays the greater the percentage of it scattered by unit mass. The exponential law of the absorption of primary γ-rays is discussed, and it is deduced that γ-rays absorbed exponentially are hardened by any material of higher atomic weight, whereas rays exponentially adsorbed by a heavy material like lead, are softened by substances

of lower atomic weight, due to the production of a larger proportion of scattered radiation. F. S.

Analysis of the γ-Rays from Radium-*D* and Radium-*E*. ERNEST RUTHERFORD and H. RICHARDSON (*Phil. Mag.*, 1913, [vi], **26**, 324—332).—Owing to the minute amount of γ-radiation given by radium-*D* and -*E*, and to the fact that the β-rays excite in heavy elements secondary γ-rays in greater amount than the primary radiation, the active preparations containing the minimum quantity of impurity were tested on filter paper or glass or aluminium. They were separated from old radium preparations by known methods. Radium-*E* was removed from the solution of -*D* and -*E* by nickel, and volatilised on to aluminium, radium-*D* and a few mg. of added lead being precipitated with aluminium by ammonia. The absorption curves of the γ-radiation in aluminium, β-rays being removed by an electro-magnet, were taken in an electroscope filled with a mixture of methyl iodide vapour and hydrogen. The γ-rays of radium-*E* are very weak in intensity compared with those of radium-*D*, and the same curve is obtained for pure -*D* as for -*D* and -*E* together. The greater part of the γ-rays of radium-*D* is exponentially absorbed ($\mu = 45$) in aluminium, and the absorption for this type is complete in about 1 mm. of aluminium. About 7% of the total ionisation is due to a second more penetrating type also exponentially absorbed ($\mu = 0.99$). Absorption is similar in carbon, and the proportion of the two types remained the same. The total γ-rays gave about nineteen divisions per minute. From radium-*E* a γ-radiation giving only 0·5 div. per minute was obtained. As nearly as could be seen it was homogeneous, and identical with the softer type given by radium-*D*, but that it was not due to the latter was shown by the fact that it decayed to zero with the period of radium-*E*. For similar β-radiations, the γ-rays of radium-*D* were some two hundred times greater than those of radium-*E*. The soft γ-radiations of radium-*D* and -*E* are probably the characteristic radiations of the *L* series to be expected of an element of atomic weight 210. F. S.

The Spectro-analytical Proof of Molecule Canal Rays. JOHANNES STARK (*Ber. Deut. physikal. Ges.*, 1913, **15**, 813—820).—A method is devised for detecting the presence of molecule canal rays in addition to the atom canal rays. By means of this method the author has been able to detect the presence of H_3 canal rays, and this confirms the existence of H_3 molecules which he is of the opinion are identical with Thompson's X_3. J. F. S.

Uni- and Multi-valent Canal Ray Lines of Aluminium, Argon, and Mercury. JOHANNES STARK, GEORG WENDT, H. KIRSCHBAUM, and R. KÜNZER (*Ann. Physik*, 1913, [iv], **42**, 241—302. Compare this vol., ii, 546).—The canal-ray spectra of aluminium, argon, and mercury are examined with the object of determining the nature of the carriers to which the different lines owe their origin. It is shown that aluminium gives rise to uni-, bi-, and ter-valent positive

atom ions in front of the cathode, and therefore gives rise to canal rays of three different velocity regions. When the potential fall at the cathode is less than about 8000 volts, the number of uni- and bi-valent aluminium atom ions in the canal rays behind the cathode far exceeds that of the tervalent aluminium ions, but above 8000 volts tervalent ions are readily obtainable in the canal rays. The univalent ions are the carriers of the doublet λ 3961·7—3944·2 Å; the bivalent ions are the carriers of the line $\lambda = 4663 \cdot 5$ Å, and the lines $\lambda = 4529 \cdot 7$, $\lambda = 4513 \cdot 0$, $\lambda = 4480 \cdot 0$ Å belong to the tervalent ions. The lines of the red argon spectrum are due to univalent positive argon ions; the visible lines of the blue argon spectrum are mainly due to bivalent positive ions, although a small number are to be attributed to the positive tervalent ions. During the emission of variable intensities, a movable equilibrium is set up between the uni-, di-, and ter-valent argon ions. Slow-moving cathode rays give rise to univalent ions by their collisions; rapidly-moving cathode rays are responsible for bi- and ter-valent argon ions. The mercury doublet $\lambda = 2847$—2224 Å is caused by the univalent mercury atom ions, whilst the first and second subsidiary mercury series of triplets are occasioned by the positive bivalent mercury ion. The lines λ 4916, 4339, 4347, 4109, and 4078 Å belong to the spectrum of the tervalent mercury ions, and the very intensive lines λ 4797, 4707, 4486, and 4398 Å are due to the positive quadrivalent mercury ions. The line λ 2536·7 Å, which is probably the first member of a series of single lines, belongs to the spectrum of the neutral mercury atom. Mercury canal rays in either hydrogen or helium contain chiefly uni- and bi-valent positive rays, and very few tervalent rays when the cathode potential fall is less than 8000 volts. With a cathode potential fall of 15,000 volts and over, there are a large number of tervalent rays and some quadrivalent rays. Under special conditions an equilibrium is set up between the neutral canal rays and the uni-, bi-, ter-, and quadri-valent canal rays. J. F. S.

Electron Affinity at the Collision Ionisation of Atoms in Chemical Compounds. JOHANNES STARK (*Ber. Deut. physikal. Ges.*, 1913, **15**, 809—812).—A theoretical paper, in which it is shown from many examples that when canal rays cause the formation of a positive atom ion by their collision with a chemical compound of an electropositive element with an electronegative element, it is generally the electropositive element which forms the ion.

J. F. S.

The Unstable Nature of the Ion in a Gas. RICHARD D. KLEEMAN (*Proc. Camb. Phil. Soc.*, 1913, **17**, 263—279).—A number of experiments are described on ionisation by collision with negative ions. The experiments were conducted in the vapours of ether, ethyl propionate, methyl butyrate, carbon tetrachloride, ethyl chloride, chloroform, pentane, benzene, acetaldehyde, methyl formate, methyl bromide, methyl iodide, ethyl bromide, ethyl iodide,

and carbon disulphide, and in the gases acetylene, hydrogen, oxygen, nitrous oxide, carbon dioxide, and air. It is shown that the ratio of the number of free ions to clusters is independent of the pressure. The ratio mentioned is obtained from the ratio of the abscissæ at a common ordinate of two curves *A* and *B*. The curve *A* being obtained with the ions drawn through the gauze screen from the space adjacent to its lower side, *B* was obtained after placing a quantity of radium near the chamber. The majority of the gases and vapours mentioned above gave the same value for the ratio, carbon tetrachloride, carbon disulphide, benzene, air, oxygen, chloroform, and hydrogen giving ratios considerably greater. The behaviour of ion clusters in gaseous mixtures is considered theoretically. J. F. S.

The Emission of Electrons by Platinum, and the Origin of the Activity of Oxide Electrodes. KARL FREDENHAGEN (*Ber. K. Sachs. Ges. Wiss. Math.-phys. Kl.*, 1913, **65**, 42—74).—A continuation of work (A., 1911, ii, 571; 1912, ii, 517) on the emission of electrons by heated metals, and the effects of heating platinum and calcium in the presence of an oxidising agent (fuming nitric acid) to a high temperature in a vacuum are now described. F. M. G. M.

Ions from Hot Salts. OWEN W. RICHARDSON (*Phil. Mag.*, 1913, [vi], **26**, 452—457. Compare Abstr., 1911, ii, 9, 10, and 1051; Davisson, 1912, ii, 116).—The salts were examined chiefly to determine e/m, and in consequence the molecular weight of the emitted ions. For zinc iodide freshly heated, the ions had an "electric atomic weight" (atomic weight divided by number of charges) 31·6 corresponding with Zn_{++}, lower values being obtained after prolonged heating. For cadmium iodide there is an emission of Cd_{++} lasting for some hours, followed by the emission of K_+ and Na_+ in turn, the temperature being from 500° to 930° Pt. Strontium iodide at about 1200° gave Sr_+, ferric chloride at 518° gave only ions corresponding with K_+, and manganous chloride between 878° and 962° gave ions of which the electric atomic weight increased from 33·9 to 79·4, and then decreased to 39·2, due probably to a mixture of K_+ and Na_+ with $MnCl_+$ and possibly Mn_{++}.

The negative ions emitted by salts at relatively low temperatures are mixtures of electrons and heavy ions, whereas all the negative ions from platinum are electrons. For calcium iodide the proportion of the current carried by the negative electrons was 0·375 at 292°, 0·734 at 315°, rising to above 0·9 at 365°. The electric atomic weight of the heavy negative ions was 120, indicating that they were I_-. When left cold in a vacuum (0·001 mm.) calcium iodide loses its power of emission of negative ions, although it recovers it when exposed to air at higher pressure, as well in dried air as in ordinary air. Strontium iodide and barium iodide gave results very similar to calcium iodide. Calcium bromide gave a less copious emission than the iodide and fluoride, but the numbers

obtained pointed to Br_- as the ion emitted. Calcium fluoride gave a large proportion of electrons even at low temperature, and the value, 97, obtained for the electric atomic weight of the heavy ions may not be accurate. In every case the deviations from the calculated value for the ions to which the results were attributed were in such a direction as to point to an undiscovered common impurity giving ions of the value of about 100 for the electric atomic weight.
F. S.

The Use of Calcium Hydride for the Autogenous Reduction of "Crude Sulphate" in the Preparation of Radium and Mesothorium. Erich Ebler and W. Bender (*Zeitsch. anorg. Chem.*, 1913, **83**, 149—158).—The absolutely dry sulphate, powdered as finely as possible, mixed with equally finely powdered calcium hydride, is pressed into a crucible and fired, as in the thermite process, by magnesium ribbon and a priming mixture. The reaction occurs with violence, and the liberated hydrogen burns off in a few minutes. Since silica is not reduced under these conditions only the quantity of calcium hydride is added necessary to reduce the sulphates present. The more lead sulphate present the more violent is the reduction, and mixtures with more than 20% are dangerous in large quantity. The product is stirred as quickly as possible into hot dilute hydrochloric acid free from sulphuric acid, and the hydrogen sulphide expelled rapidly by boiling. If lead is present normal acid is used in which lead sulphide is insoluble, the residue being repeatedly re-extracted. In absence of lead, $5N$-acid is employed. From the solution, the barium–radium chloride is precipitated in pure state by passing in hydrogen chloride, until three-fourths of the barium chloride, containing all the radium, is precipitated. In trials with crude sulphate from carnotite, equal parts of hydride and sulphate were employed, the extracted barium chloride weighed 37% of the raw material, and contained 80·5% of the radium present. In trials with a poor lead-free crude sulphate, from a vanadium and copper containing chalcolite from Ferghana (Turkestan), two-thirds of the weight of hydride was used; the extract weighed 24% of the raw material, and contained 86·2% of the radium present. The reduction of the sulphate is extraordinarily complete, and the method shortens the process of extracting the radium considerably. The calcium hydride (from Elektrochemische Werke, Bitterfeld) is powdered in a steel ball mill, and contains then 80% of calcium hydride. F. S.

Method for the Determination of Radium in Radioactive Substances. Arnold L. Fletcher (*Phil. Mag.*, 1913, [vi], 26, 674—677).—In this method, by an adaptation of the micro-furnace, a small, splintered and weighed fragment of the mineral or salt (from 0·01 to 0·0001 gram) is placed in a hollow in a thin carbon rod, and raised for ten to thirty seconds to a temperature between 2000° and 3000° inside a small chamber provided with a rubber balloon to allow for the expansion and generation of gas. Afterwards the contents of the chamber are drawn into an exhausted

electroscope in the usual way. Trials with small quantities of different minerals gave concordant results, and the method has the great advantage that it does not require the use of chemicals. Experiments showed that the rapid escape of emanation from heated minerals does not begin until 750°, and de-emanation is complete at bright redness. F. S.

Distribution of the Active Deposit of Radium in an Electric Field. II. EDWARD M. WELLISCH (*Phil. Mag.*, 1913, [vi], 26, 623—635; *Amer. J. Sci.*, 1913, [iv], 36, 315—327. Compare Abstr. 1912, ii, 521).—As the result of this investigation, the amount of active deposit settling on the cathode appears to reach a definite limiting fraction of the total with large potentials, but columnar recombination of the positively charged active deposit particles with negative ions reduces the amount for smaller potentials, whilst volume recombination operates for very small potentials. The recoil atom in its passage through the gas produces a great number of ions, and under these conditions the atom may lose its positive charge, but the proportion so discharged is not influenced by the electric field or the pressure of the gas, which affect the columnar and volume part of the recombination. There is evidence that the recoil atoms differ from ordinary positive ions, more readily suffering recombination, which possibly is connected with their larger mass. This is especially the case with moist gases, but the difference is well marked in gases dried with all care. Owing to its larger mass and slower motion of diffusion the recoil atom escapes from the column of ions it produces less readily than the positive ion. The limiting value to the percentage cathode activity depends on the nature of the gas. This is shown by experiment to be specially small (10%) in ethyl ether, which is ascribed to the ease with which the molecules of this substance are ionised. F. S.

The Distribution of the Active Deposit of Actinium in Electric Fields. H. P. WALMSLEY (*Phil. Mag.*, 1913, [vi], 26, 381—401).—Using special precautions to eliminate dust and the accumulated active deposit products from the gas, it was found that the actinium active deposit distributes itself exponentially along the length of a negatively charged wire, stretched axially through a tube along which an air stream carrying the emanation is passing, and therefore that the ratio of the deposits on the cathode and anode is independent of the concentration of emanation in the gas. By measuring the variation with voltage of the active deposit, both when the wire was charged positively and negatively, it was shown that the anode activity decreases and the cathode activity increases with increase of voltage, and hence that none of the active deposit atoms carry a negative charge. The measurements were found to conform to the view that the actinium-*A* atoms acquire a positive charge during their creation from the emanation, and then are subject, like positive ions, to neutralisation of the charge by recombination with negative ions in the gas.

But in circumstances when the whole of the actinium-*A* is transformed during the passage to the electrode and the whole deposit reaches the electrode as actinium-*B*, recombination continues, which renders it extremely probable that actinium-*B* also acquires a positive charge at the moment of its creation. External ionisation of the gas increases the amount of uncharged active deposit, and the proportion deposited on the anode, as is the case with the radium active deposit. The effects of dust particles and large ions in the gas in increasing the anode activity were also studied.

F. S.

Preparation of Radioactive Substances from Thorium. FRITZ GLASER (*Chem. Zeit.*, 1913, **37**, 1105—1106. Compare this vol., ii, 465).—The presence of lead sulphate is an advantage in the separation of thorium-*X* from monazite sand, thorium, etc., as the radioactive substance is absorbed by the lead sulphate. When the lead is subsequently separated as sulphide, the radioactive substance remains in solution. Radioactive substances may also be prepared from mesothorium, barium salts being added before the original monazite sand is decomposed with sulphuric acid in order that the substances may be concentrated with the barium sulphate.

W. P. S.

The Distribution of the γ-Rays among the Single Products of the Thorium Series. LISE MEITNER and OTTO HAHN (*Physikal. Zeitsch.*, 1913, **14**, 873—877).—Thorium-*X* was freed from its subsequent products by ignition three times in a platinum dish, and showed initially less than 0·2% of the equilibrium amount of thorium-*C*. The initial radiation was taken in a β-ray electroscope through a variety of thicknesses of aluminium foil. It was found that the ratio of the final equilibrium activity to the initial activity reached a maximum for 0·5 mm. aluminium, which corresponds with the complete absorption of the soft β-rays of thorium-*X*, then diminished as the equilibrium β-rays of thorium-*D* are absorbed, and finally increased for greater thicknesses, namely, 2·5 mm. aluminium, and 0·7 mm. of lead. This indicates that thorium-*X* emits a γ-radiation more penetrating than the β-rays, and less penetrating than the γ-rays of thorium-*D*.

Thorium-*B* was shown to give a γ-radiation by comparing the α- and γ-ray recovery curves of an initially pure preparation. The α-ray curve rose from zero, but the γ-ray curve rose from an initial value about 22% of the maximum activity, as measured without screens, except the 2 mm. thick brass wall of the γ-ray electroscope. These γ-rays are much more easily absorbed than those of thorium-*D*, and are reduced to half-value in about 1 mm. thickness of lead.

Thorium-*C* gives the greater portion of the β-rays of thorium-*C* and -*D*, and these are of a harder type than those of thorium-*D*, but the latter gives practically all the γ-rays (A., 1912, ii, 514). Two preparations of pure thorium-*C*, obtained by deposition on a nickel foil which was cut in half, were examined for the recovery

curve of γ-rays through different thicknesses of lead. The two recovery curves were of the same form, proving that if thorium-*C* emits any γ-radiation at all, its penetrating power, between 0 and 19 mm. of lead, is identical with that of the γ-radiation of thorium-*D*. F. S.

Some Experiments with the Active Deposit of Thorium. ERNEST MARSDEN and R. H. WILSON (*Phil. Mag.*, 1913, [vi], **26**, 354—361).—The question whether thorium-*C* consists of two separate products, or of one product disintegrating dually in two ways, was investigated by finding whether during the decay of the radiation of thorium-*C*, separated from a solution by means of a nickel plate, the α-rays of range 4·8 cm. decayed at a different rate from those of range 8·6 cm. This was done by balancing in two ionisation chambers the current due to the latter part of the range of the rays of longer range against the first part of the range of both rays together. No alteration of balance occurred as the radiations decayed, and it was deduced that if thorium-*C* consists of two separate products, their periods must be the same to within 1 part in 570.

A repetition of the experiments of Meitner (A., 1912, ii, 723) confirmed the results, but it was found that thorium-*C*, which, when deposited from the emanation on a wire, is not volatile below 700° in air, is appreciably volatile when evaporated from a hydrochloric acid solution and heated gently, not above 300°. From a nitric acid solution no volatilisation occurs. In presence of stannous chloride, zinc chloride, or even ammonium chloride, practically the whole may be volatilised with the fumes of the added salt. It appears that the differences observed by Meitner in the α and γ-ray recovery curves of thorium-*B* are to be ascribed to more complete volatilisation of thorium-*C* from the single drop of α-ray preparation than from the larger quantity of γ-ray preparation. Other experiments showed that no true separation of the two sets of α-rays from thorium-*C* had been effected. Experiments with the β-rays of thorium-*C* showed that the product giving these rays could not be separated from the parent of thorium-*D*.

A soft γ-radiation was found to be emitted by thorium-*B* analogous to that recently discovered for radium-*B*. F. S.

The Position where the Thorium Series Branches. P. BEER and KASIMIR FAJANS (*Physikal. Zeitsch.*, 1913, **14**, 947—951. Compare preceding abstract).—The absorption curves of the α-rays from thorium-*C* separated by nickel from the solution of the active deposit, both with and without the use of stannous chloride, were found to be identical, whereas if Meitner's explanation were correct, a difference should have been observed. Similarly, the absorption curves of the β-rays were identical. Meitner's results were traced to the volatility of thorium-*C* chloride in presence of stannous chloride. The greater volatility of the *C*-product than the *B*- in form of chloride, and the lesser volatility in form of metal or oxide, is in accord with the fact that the *C*-product is analogous to

bismuth, and the B-product to lead. Experiments with radium-E, which is chemically identical with thorium-C, showed that in absence of stannous chloride it is quantitatively precipitated on nickel; in presence of stannous chloride only 10% is separated. These observations support the scheme of Marsden and Darwin that the branching of the thorium series occurs at the C-member, and remove all the objections to it. F. S.

The Branching Relations and Atomic Weights of the C-Members of the Three Disintegration Series. KASIMIR FAJANS (*Physikal. Z-itsch.*, 1913, **14**, 951—953. Compare this vol., ii, 660).—It is shown that the products, actinium-C, thorium-C, and radium-C, which disintegrate dually along two branches, conform to the previous generalisation. The separate periods of the α-modes of disintegration are respectively 2·15 minutes, 2·87 hours, 45 days, and the estimated atomic weights, 210·5, 212·4; and 214·5. The separate periods of the β-ray modes of the two latter are 1·55 hours and 19·5 minutes. In the same place in the periodic table is radium-E, with atomic weight 210·5, and β-ray period five days, which also conforms. F. S.

Range of the Recoil Atoms from Thorium-C and Actinium-C. A. B. WOOD (*Phil. Mag.*, 1913, [vi], **26**, 586—597).—In the first method the active deposit on a small platinum disk was placed at the centre of a hemisphere, lined with tin foil, and kept charged positively to the disk. Recoiled atoms of thorium-D or actinium-D reached the hemisphere at low pressures by virtue of their momentum, whereas those just failing to reach were drawn back to the source by the action of the field, which was not sufficiently intense appreciably to affect the range of the recoil atoms. Dust and moisture had to be eliminated. The amount of recoil product was measured in a β-ray electroscope, and curves plotted of the amount for different pressures of air and hydrogen. The amount fell off with increasing pressure to about 4 mm. pressure (of air), and then remained constant at a small value, due probably to diffusion of recoil atoms which have become discharged *en route*. By extrapolation, it was estimated that the maximum range of the recoil atoms of thorium-D is 0·12 mm. in air at *N.T.P.*, and in hydrogen rather more than four times longer. For actinium-D the range was found to be almost exactly the same, indicating that thorium-D is produced in the change of thorium-C in which an α-particle of range 4·8 cm. is emitted (that of actinium-C being 5·4 cm.), and not in the change of thorium-C in which the α-particle of range 8·6 cm. is expelled, in agreement with the accepted view. The recoil atoms showed marked lack of homogeneity, due either to irregularities in the surface of the plate from which they recoil, or to scattering in their passage through the gas.

In the second method, the ionisation produced by the recoil atoms was measured at different pressures in an apparatus analogous

to that used by Bragg for determination of α-ray ranges. After correction for ionisation due to α-rays and for δ-rays, the curves connecting the ionisation per mm. of pressure and the pressure was found to be of the same form for actinium-C as that connecting the amount of recoil product with pressure in the first method. But for thorium-C a marked difference was observed, indicating that in addition to thorium-D there is a second inactive recoil product of longer range capable of producing ionisation, and corresponding with the change of thorium-C associated with the 8·6 cm. range α-particle. The range of this recoil product was estimated to be 0·175 mm. in air, and 0·74 mm. in hydrogen, in agreement with Wertenstein's conclusion that the ranges of recoil products are proportional to the ranges of the α-particles expelled in the same change. F. S.

Uranium-X_2 the New Element of the Uranium Series. KASIMIR FAJANS and O. GÖHRING (*Physikal. Zeitsch.*, 1913, **14**, 877—884).—Since the product of a β-ray change is electrochemically nobler than its parent, it is to be expected that uranium-X_2 would be easier to separate electrochemically than uranium-X_1. Separation was effected by immersing polished lead plates for a minute in a feebly acid solution of uranium-X containing iron. Decay curves are shown, from which it is deduced that the mean value of the half-period was 1·15 minutes ($\pm$0·01), and the period of average life 100 seconds. Since uranium-X_1 is analogous to thorium and uranium-X_2 to tantalum, the precipitation of tantalic acid by acidifying a solution of potassium hexatantalate was tried to effect the separation. Uranium-X_2 is nearly quantitatively precipitated without uranium-X_1, when an acid solution of uranium-X, containing thorium, is added to an alkaline solution of potassium hexatantalate. With such preparations it was shown that uranium-X_2 emits only the hard type of β-rays given by uranium-X. From the recovery-curve of the β-rays of uranium-X_1, prepared, free from uranium-X_2, by precipitation of thorium-uranium-X in acid solution with hydrofluoric acid, it was shown that uranium-X_2 gives practically no hard β-rays. It could not be shown experimentally that uranium-X_1 gives the soft β-rays and uranium-X_2 the γ-rays, as may reasonably be inferred. F. S.

The Disintegration of Uranium-X. ALEXANDER FLECK (*Phil. Mag.*, 1913, [vi], **26**, 528—535. Compare preceding abstract).—The existence of the uranium-X_2 of Fajans and Göhring has been confirmed. It is deposited from slightly acid solution of uranium-X on lead, in small amount on zinc and magnesium, but not on gold or platinum. The hard β-radiation of the lead plate fell, in six or seven minutes, to the practically constant value of 60 or 80% of the value as first measured, from one and a-half to two minutes after removal from the solution. It is precipitated in excess of the equilibrium amount with lead chloride, bismuth oxychloride, lead or bismuth sulphide, when these precipitates are formed in a solution of uranium-X. On the other hand, a precipitate of lead

sulphate contains initially less than the equilibrium amount of uranium-X_2, and from such a preparation the recovery curve of the hard β-rays was obtained. Precipitates of barium or thorium oxalate appear to be similar. By comparing the hard and soft β-rays from such a precipitate of lead sulphate, it was shown that the soft β-radiation comes from the parent substance, uranium-X_1, of period of average life 35·5 days, whilst the hard β-radiation comes from the product, uranium-X_2. The mean value found for the period of average life was 1·6 minutes, corresponding with the half-period 1·1 minutes. In one experiment with bismuth oxychloride, which could not be repeated, 94·5% of the equilibrium amount of uranium-X_2 was removed. It could not be volatilised at all under any conditions, even when evaporated and ignited with hydrofluoric acid or acid potassium fluoride, although under these conditions tantalum is more volatile than niobium. It has not been found possible to obtain a definite proof that it occupies the predicted place in the periodic table as "eka-tantalum."

F. S.

The Existence of Uranium-*Y*. GEORGE N. ANTONOV (*Phil. Mag.*, 1913, [vi], **26**, 332—333).—Controversial against Fleck (this vol., ii, 464), claiming that the existence of uranium-*Y* has not been disproved.

F. S.

Emission of Electrons from Tungsten at High Temperatures: an Experimental Proof that the Electric Current in Metals is Carried by Electrons. OWEN W. RICHARDSON (*Phil. Mag.*, 1913, [vi], **26**, 345—350; *Physikal. Zeitsch.*, 1913, 14, 793—796).—The view that the emission of electrons from heated solids is invariably a secondary effect accompanied by traces of chemical action is combated. Tungsten filaments, surrounded by a concentric cylindrical electrode of copper gauze, were heated in a high vacuum, special methods being employed to remove absorbed gases and volatile impurities. The number of electrons emitted by the glowing filament was compared with the number of molecules of gas emitted, as deduced from the rise of pressure of a gauge attached, and found to be from 5 to 200 million times greater. It is also many thousand times greater than the calculated number of impacts of gas molecules upon the filament. The possibility that the emission is connected with the slow evaporation of the tungsten was negatived by the fact that, per atom of tungsten so lost, about a million electrons are emitted. In some circumstances the mass of the electrons emitted exceeds the mass of the tungsten lost, and amounts to 4% of the total mass of the tungsten. The possibility that condensable vapours, not measured by the gauge, may cause the emission is negatived by the fact that liquid air and charcoal do not affect the emission, which is not affected by very considerable changes in the amount and nature of the gases and vapour present. It is not denied that under other circumstances electrons may be emitted from metals by the action of chemical reagents, and that this emission would follow the same

law of dependence on temperature. The experiments prove that the current in metals must be carried by electrons entering the metal from outside points of the circuit. F. S.

The Helium Content and Radioactivity of Natural Gas. Emerich Czakó (*Zeitsch. anorg. Chem.*, 1913, **82**, 249—277. Compare Cady and McFarland, A., 1907, ii, 949).—Natural gas is examined in a special apparatus, in which hydrocarbons are condensed by liquid air, and other gases are removed by means of cooled charcoal. All the gases examined are found to contain helium, the percentages in natural gas being 0·0014 from Kissármás (Hungary), 0·0063 from Pechelbronn, 0·0089 from Wels (Austria), and 0·0141 from Neuengamme near Hamburg; also 0·0067 in a mine gas from Gneisenau, and 0·38 in gas from a deep boring in Alsace, the last containing 46% of nitrogen, whilst the others are low in nitrogen. Atmospheric air contains about 0·0005% of helium, and calculations are given of the quantity passed daily into the atmosphere from some of the principal thermal springs and sources of natural gas.

The radioactivity of the same gases is determined by means of the fontaktoscope. All the gases examined contain emanation, the quantity being small, and varying within rather narrow limits. The deep boring in Alsace gives a very high activity, the primary rock being reached in this case, whilst the other borings are in sedimentary rocks. An approximate proportionality between activity and helium content is observed. The quantity of helium is, however, far too large to be derived entirely from the recent disintegration of radium, and the greater part must have been present previously in the rocks. C. H. D.

An Occurrence of Radioactive Minerals. W. Mironov (*Zeitsch. Kryst. Min.*, 1913, **52**, 619; from *Sitzungsber. Naturf. Ges. St. Petersburg*, 1910, No. 7—8, 286—290).—Radioactive minerals occur in a granular limestone of Devonian age at Tyuya-Muyan, 30 versts south-east of Andijan in Fergana, Russian Central Asia. One of these minerals—ferganite—has a radioactivity of 1·44, compared with thoria as 1, and Joachimsthal pitchblende as 1·82. L. J. S.

Occluded Gases in Geissler Tubes. Robert W. Lawson (*Physikal. Zeitsch.*, 1913, **14**, 938—941).—The author has extracted the gases found in Geissler tubes, some of which were new, and some of which had been used for prolonged periods. He draws the conclusion from the experiments that all the gases observed had been occluded in the electrodes, and that the formation of helium from hydrogen is not confirmed by his experiments. In the same way the synthesis of neon from helium and oxygen is unlikely, since helium was present long after the neon; and oxygen was only observable when the tube had been in use for several hours. The author attributes the relatively large amount of oxygen to the decomposition of neon into helium and oxygen (compare Collie and Patterson, T., 1913, 419). J. F. S.

Electrochemistry of the Halogens, Chlorine, Bromine, Iodine and of Iodine Monochloride, Iodine Bromide, and Iodine Trichloride in Nitrobenzene Solution. LUDWIK BRUNER and ANTONI VON GALECKI (*Zeitsch. physikal. Chem.*, 1913, **84**, 513—557).—A large number of conductivity experiments have been carried out with solutions of the above-mentioned substances and hydrogen bromide in nitrobenzene solution. It is shown that the conductivity differs as absolutely dry nitrobenzene or nitrobenzene which has been exposed to the air is used. The various solutions were therefore in many cases prepared and measured in entire absence of moisture and out of contact with air. In perfectly dry nitrobenzene, chlorine, bromine and iodine do not conduct electricity, whilst iodine trichloride and iodine bromide possess considerable conductivity. In moist solutions of nitrobenzene, iodine, bromine, bromine iodide and iodine trichloride all conduct, the conductivity increasing in the order in which they are written above. Dilution of the solutions causes an increase in the equivalent conductivity. On electrolysis, both in dry and moist nitrobenzene solutions, the halogen is always deposited on the anode in accordance with Faraday's law. The electrodes in these experiments were of silver which had been coated with a silver haloid, and consequently were not affected by coming into the halogen solutions. The amount of electrolysis was determined by an increase in the weight of the anode due to further formation of silver haloid. There was no deposition on the cathode but in some cases a slight reduction occurred. Continued electrolysis caused complete removal of the halogens from the solution. In transport experiments the halogens wandered entirely to the anode, the quantity of the halogen round the anode corresponded with two equivalents for every 96,540 coloumbs passed through the solution except in the case of bromine, where the relationship is smaller, and varied between 1·5—1·7 equivalents. The nature of the conductivity in these cases is discussed, and it is shown that it is not due to the presence of halogen acids or to an ionisation of the halogens $ICl \longrightarrow I^{\cdot} + Cl'$. An explanation is offered based on the formation of additive compounds of the oxonium type with the solvent, thus $C_6H_5\cdot N\ll^{O=ICl}_{O=Cl_2}$. Measurements are also given of the conductivity and transport of hydrogen bromide in dry nitrobenzene solution. J. F. S.

The Variations in the Electrical Conductivity of Nitrobenzene Solutions of Bromine. LUDWIK BRUNER and J. SAHBILL (*Zeitsch. physikal. Chem.*, 1913, **84**, 558—569. Compare preceding abstract). —The influences which may bring about a fluctuating conductivity in solutions of nitrobenzene have been studied. It is shown, in the first place, that the addition of water is not responsible entirely for the changes. On distilling nitrobenzene, four fractions were obtained, each extending over a range of 0·25°; the first of these gave a solution with bromine which had a conductivity value six times as large as that of the last fraction. On freezing a solution

of bromine in nitrobenzene and then raising to the experimental temperature, the conductivity rises permanently. The addition of several oxides (Ag_2O, Al_2O_3, and CdO) reduce the conductivity of a bromine solution about seventy-five times. Other substances, such as silica and barium sulphate, have no action. A hypothesis to explain the changes of conductivity is given. This is based on the formation of conducting additive compounds and an absorption of these conductors by the added oxides. J. F. S.

The Electrical Conductivity and Electrolysis of Solutions of Bromine, Iodine Bromide, Iodine Chloride and Iodine Trichloride in Liquid Sulphur Dioxide. LUDWIK BRUNER and E. BEKIER (*Zeitsch. physikal. Chem.*, 1913, 84, 570—584. Compare preceding abstracts).—Experiments similar to those of Bruner and Galecki (*loc. cit.*) in nitrobenzene solution have been carried out in sulphur dioxide solution. It is shown that liquid sulphur dioxide which has been carefully dried by distilling over phosphoric oxide has no conductivity. A solution of bromine has no conductivity in the absence of moist air, but as soon as moisture is admitted to the apparatus a considerable conductivity is set up. The conductivities of the halogen compounds mentioned above have been measured in sulphur dioxide solution, and it is shown that the equivalent conductivity in each case is about one hundred times smaller than that given by Walden. In the latter cases the authors attribute the conductivity to the formation of conducting additive compounds with the solvent. From electrolysis experiments it is shown that the halogens are deposited on the anode, and that there is no evidence of the existence of a halogen acting as cation in sulphur dioxide solution. J. F. S.

Electrical Conductivity of Dilute Solutions of Some Sodium Salts in Ethyl Alcohol. NILRATAN DHAR and DEVENDRA NATH BHATTACHARYYA (*Zeitsch. anorg. Chem.*, 1913, 82, 357—360).—The value of μ_∞ for sodium benzoate and other organic salts in alcohol is less than 40, whilst for inorganic sodium salts it approaches 45. C. H. D.

Electrical Conductivity of Solutions of Molybdenum Pentachloride. STEWART J. LLOYD (*J. Physical Chem.*, 1913, 17, 592—595).—Molybdenum pentachloride dissolves in organic solvents, forming solutions which have a greenish- or a reddish-brown colour. The solutions with a green colour show a decrease in molecular conductivity on dilution, whilst the reddish-brown solutions either do not conduct appreciably or show an increase in molecular conductivity when diluted. In the case of the acetone solutions which are of a deep green colour, the conductivity decreases on dilution, passes through a minimum, and on further dilution increases. This change in the character of the conductivity-dilution curve is not accompanied by any corresponding change in the colour of the solutions. Data are recorded for solutions in methyl and ethyl acetate, acetone, benzaldehyde, pyridine, and glycerol. H. M. D.

A General Relation between the Concentration and the Conductivity of Ionised Substances in Various Solvents. CHARLES A. KRAUS and WILLIAM C. BRAY (*J. Amer. Chem. Soc.*, 1913, 35, 1315—1434).—The authors propose to express the relation between the concentration and the conductivity of electrolytic solutions by the general equation: $(c\gamma)^2/c(1-\gamma)=K+D(c\gamma)^m$, where c is the concentration, γ the conductivity ratio Λ/Λ_0, and K, D, and m are constants. In sufficiently dilute solutions, the term involving $(c\gamma)^m$ becomes negligible in comparison with K, and the equation approaches the simple mass-action law as a limit. In concentrated solutions K becomes negligible in comparison with $D(c\gamma)^m$, and the equation assumes the form of that of Storch. For $m>1$ the molecular conductivity passes through a minimum value, whilst for $m<1$ the molecular conductivity decreases continuously with increasing concentration.

At first glance it may appear that the proposed equation is a purely arbitrary one, involving four constants, Λ_0, D, K, and m (Λ_0 being involved in the determination of γ). The constants, however, are not arbitrarily determined in all respects. K and Λ_0 are, of course, interdependent, but they may in most cases be determined independently of D and m. In many cases m may be determined independently of the three remaining constants. Graphical methods are described whereby the constants may be conveniently evaluated from the experimental data. It is also shown that a method is provided whereby the law of mass action may be tested without assuming a value for Λ_0, a result of very great importance.

The general equation was tested on, and found to apply to, the extensive conductivity data which have been accumulated by Franklin and his co-workers for solutions in liquid ammonia. The deviations from the law of mass action become appreciable at ionic concentrations between $0{\cdot}001N$ and $0{\cdot}0001N$. The smaller the ionisation of the electrolyte the higher the total concentration up to which the law of mass action is sensibly obeyed.

With the aid of the transference data of Franklin and Cady (A., 1904, ii, 466) the ionic velocities of a considerable number of ions in liquid ammonia solutions have been calculated, and these values compared with those of the same ions in water. The former are, on the average, 2·59 times greater than the latter, although the ratio is by no means constant. It is noteworthy that the velocity of the ammonium ion is not larger than that of the other cations in liquid ammonia, and from this result and other considerations the conclusion is drawn that the speed of certain ions in a given solvent is not related to the possible dissociation of this solvent into ions of the same character as those of the dissolved substance.

The general equation is also found to apply to solutions in liquid sulphur dioxide. The influence of temperature on the conductivity of these solutions is readily accounted for by the variation which these constants undergo with change in temperature.

In the case of dilute solutions of strong electrolytes in non-aqueous solvents (including the higher alcohols), conductivity measurements on which have been made by Dutoit and his co-workers, it was found that the law of mass action applies, within the limits of experimental error, up to ionic-concentrations between 0·0001 and 0·001 normal; at higher concentrations the deviations become measurable. This limiting ionic concentration is approximately the same for solutions of a given electrolyte in different solvents, and for different electrolytes, strong or weak, in the same solvent.

In the case of concentrated solutions in solvents of low ionising power, γ may be neglected in comparison with 1, and the general equation simplifies to $c\Lambda^2=P(c\Lambda)^m$, where P is a constant involving Λ_0. Since Λ_0 does not occur explicitly in this equation, the general equation may be tested without a knowledge of the value of this constant. The equation was found to hold for all cases (sixty-seven solutions and twelve solvents) for which trustworthy data exist.

The general equation is also applicable to aqueous solutions of strong electrolytes, for example, to solutions of potassium chloride varying in concentration from 0·001 to 2·0 normal. The agreement is to within 0·1%, but to obtain this agreement in the more dilute solutions it is necessary to assume $\Lambda_0=128·3$ instead of the commonly accepted value 130·1. In all probability the commonly accepted values for Λ_0 for all binary electrolytes are 1—2% too high.

There is reason for believing that salts of higher valence type obey the same general law as do binary electrolytes, but the general equation cannot be tested as yet, owing to the lack of available data and because of complications arising from the formation of intermediate ions.

The relation between the ionising power of a solvent and the values of constants K, D, and m is discussed, and it is shown that, with decreasing dielectric constant, K approaches zero (or, at least, a very small value); D approaches a constant value, 0·35, which undergoes but little change as the dielectric constant falls below 22; and m increases, approaching a value greater than 2. The exceptions to the Nernst-Thomson rule lose their significance in the light of the results obtained in this paper, and when the comparison for a given solute is made between the constants of the general equation instead of between the conductivities directly, no discrepancies appear.

From a theoretical point of view the most important results obtained are: that all solutions of binary electrolytes obey the same dilution law; that the law of mass action is obeyed at high dilutions; that the divergence from the law of mass action at higher concentrations is a function of the ionic concentration; and that for a given electrolyte in different solvents the trend of the conductivity curve is determined by the dielectric constant of the solvent. Finally, it is shown that the fundamental hypothesis of Arrhenius,

according to which the ionisation is measured by the ratio Λ/Λ_∞ is in harmony with the observed facts, not only in very dilute solutions, but also in concentrated solutions (up to more than normal when viscosity changes are taken into account). An explanation of the observed deviations from the law of mass action is to be looked for in the interacting forces due to the presence of charged particles (ions) throughout the body of the solution. T. S. P.

Chemical Reactions and Electrical Conductivity of Non-aqueous Solutions. HAMILTON P. CADY and H. O. LICHTENWALTER (*J. Amer. Chem. Soc.*, 1913, **35**, 1434—1440).—Kahlenberg and others (Kahlenberg, A., 1902, ii, 301; Sammis, A., 1906, ii, 835; Gates, A., 1911, ii, 394) have conducted double decompositions in non-aqueous solutions, and state that some instantaneous reactions occur in solutions which show no conductivity, that is, in solutions where dissociation has not occurred. This statement has been disputed by Allen (*Kans. Univ. Sci. Bulletin*, 1905), and the authors have carried out further experiments on the subject.

Benzene, toluene, and light petroleum were used as solvents, the salts employed being silver melissate, copper melissate, lead stearate, barium linoleate, lead erucate, and copper oleate. In all experiments moisture was rigorously excluded.

The benzene and toluene solutions of each of these salts showed some conductivity, which increased when dry hydrogen chloride was passed into the solution. No precipitation occurred with the salts of the saturated acids, that is, with the melissates and stearates, when hydrogen chloride was passed in, but precipitates were formed with the oleates and erucates, that is, with the salts with one double bond, and with the linoleate, which contains two double bonds. In no instance was the reaction found to be instantaneous, although rather rapid; the conductivity of the solution diminished as precipitation took place. The solutions of the salts all showed the phenomenon of polarisation, which indicated that they possessed properties similar to those of an ordinary electrolyte.

It is thus possible, in contradistinction to the opinion of Kahlenberg, that the above reactions may be due to ionisation. An alternative explanation may be that the reactions with the salts of the unsaturated acids take place in two stages, additive products being first formed with the hydrogen chloride, and then breaking down into the metal chloride and the organic acid. T. S. P.

The Volume of Ions in Solution. NILRATAN DHAR (*Zeitsch. Elektrochem.*, 1913, **19**, 748—753).—On the assumption that Stokes' law is applicable to ions, the author deduces the formula

$$6\pi\zeta v/HaN = 29 \times 10^{13},$$

in which a is the radius of the ion, N the number of ions in the gram ion, v the mean velocity of the ion, H the field in which it moves, and ζ the viscosity of the solution. From investigation of this equation with a number of solutions it is shown that the ions occupy a smaller space than the molecules from which they are formed. J. F. S.

The Degree of Dissociation of Binary Electrolytes as a Function of the Normality. CORNELIS VAN ROSSEM (*Chem. Weekblad*, 1913, **10**, 874—876).—A theoretical paper discussing the relation between the degree of dissociation of weak and strong binary electrolytes and the normality. A. J. W.

Electrical Dispersion Bands in Benzene, Toluene, and Petroleum. ANDREI R. COLLEY (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, *Phys. Part*, 249—265).—The author shows that the method employed by Linnitschenko (this vol., ii, 550) in investigating electrical dispersion leads to considerable errors, the accuracy attained being at most one-tenth of that given by the author's method (A., 1908, ii, 909), so that Linnitschenko's criticisms of the author's results are unjustified. T. H. P.

The Potential Due to Liquid Contact. III. ALEXANDER C. CUMMING and ELIZABETH GILCHRIST (*Trans. Faraday Soc.*, 1913, **9**, 174—185).—Whilst Planck's equation applies to boundaries at which mixing does not occur, Henderson's equation applies to continuous transition through a series of mixtures. Experiments show that a "sharp" boundary is not realisable in practice, and Planck's equation is therefore inapplicable. The change of contact potential with time has been measured, and must be attributed to salt migration. In actual measurements, a boundary must be freshly prepared, and capillary tubes must be avoided.

Cells of the type $N/1KCl$|connecting solution|$N/1KCl$ have also been examined, in which the first boundary is at a membrane, and at the second the solutions mix. In all cases a potential is observed, which steadily falls to zero. C. H. D.

Thermal Calculation of Electromotive Forces. JOHANNES N. BRÖNSTED (*Zeitsch. Elektrochem.*, 1913, **19**, 754—757).—The heat of the reactions $Hg + AgCl = HgCl + Ag$ and $\frac{1}{2}Pb + HgCl = Hg + \frac{1}{2}PbCl_2$ have been redetermined, and found to have values 1400 cal. and 10,930 cal. respectively, which are in accordance with the values previously found by the author. Using the Nernst heat theorem, the electromotive force of the two elements represented by the above equations calculates out to $\pi = 0{\cdot}026$ and $0{\cdot}514$ respectively. These numbers agree well with those determined experimentally. It is shown that the heat values used by Pollitzer (this vol., ii, 669) are not in accord with those found experimentally. J. F. S.

Inaccuracy of the Copper Voltameter. NILRATAN DHAR (*Zeitsch. Elektrochem.*, 1913, **19**, 746—748).—The author gives the results of a series of determinations made with a copper voltameter in series with a silver voltameter which show that for small currents, 5—0·5 milliamperes, the copper voltameter gives values which are much too low. The results of a number of other investigators on the same subject are discussed, and it is made evident that the influence of the current density, acid concentration, and presence of air affect the accuracy of the voltameter, but in exactly which way is not clear. J. F. S.

The Electrical Transport of Gels. STANISLAUS GLIXELLI (*Kolloid-Zeitsch.*, 1913, **13**, 194—200).—Measurements have been made of the rate at which particles of stannic acid are transported when under the influence of an electrical field. The stannic acid was prepared by hydrolysis of the halogen salts of tin.

The mobility of the gel is found to be a function of the hydrogen ion concentration of the dispersive medium, the gel behaving as a negative colloid when the hydrogen ion concentration is very small, and as a positive colloid at higher concentrations. The isoelectric point corresponds with 0·00011 mol. of halogen acid per litre. The transition from the one electrical condition to the other is a reversible process, and the isoelectric point can be satisfactorily determined either by the gradual addition or by the gradual removal of acid. From experiments in which other acids were added to the dispersive medium, it has been found that the behaviour of oxalic acid is anomalous, and this is attributed to the formation of complex compounds.

An explanation of the varying electrical character of the gel particles is given, in which it is supposed that the amphoteric nature of the stannic acid plays a part. H. M. D.

The Photoelectric Effect. KARL T. COMPTON and OWEN W. RICHARDSON (*Phil. Mag.*, 1913, [vi], **26**, 549—567. Compare A., 1912, ii, 1039).—The relationship between the frequency of the light and the photoelectric emission of electrons is studied in the case of platinum and aluminium by means of an apparatus similar to that previously employed. The results indicate that the photoelectric sensitiveness is the same function of the frequency for all metals, the difference being that the curve is shifted bodily out to the region of short wave-lengths for electronegative metals. This function is evidently not expressed by the equation

$$N = Ah/R^2v^2(1 - e/300 \,.\, w_0/hv),$$

which it was proposed to test in the investigation. The equation, however, accurately predicts the values of λ_0 and $\lambda_{max.}$, and seems to express part of the truth. It had previously been shown that this equation is only one of the solutions of the theoretical equations. The present results point to the existence of another term in the solution, which would probably be found in N being equal to the sum of two terms. The first term would be the right member of the equation, and would provide the first maximum and the "selective" effect. The second term would provide the second maximum, and account for the "normal effect." J. F. S.

Photoelectric Researches on Some Liquids. Apparent Loss of Positive Electricity Caused by the Ultraviolet Rays. MICHELE LA ROSA and V. CAVALLARO (*Nuovo Cim.*, 1913, [vi], 6 ii, 39—47).—When photoelectric observations are made on feebly active substances placed very near the source of ultraviolet rays, the Hallwachs effect and the Lenard effect are superposed, so that some substances may appear active in the usual way (most rapid dispersion of the negative charge), some inactive and some active

in the opposite way (most rapid dispersion of the positive charge). The result depends on the nature of the substance and on the conditions of experiment. Water, ethyl alcohol, and ethyl acetate show the Hallwachs effect more than the other. Ethyl ether is inactive or very feebly so; methylene bromide is feebly active; in both cases the Lenard effect is greater than the other effect.

R. V. S.

Magnetic Susceptibility of Binary Alloys. KÔTARÔ HONDA and TAKÉ SONÉ (*Sci. Rep. Tôhoku Univ.*, 1913, **2**, 1—14. Compare A., 1910, ii. 686).—The magnetic susceptibility of the alloys of antimony–bismuth, antimony–zinc, antimony–aluminium, antimony–tellurium, tin–tellurium, tin–lead, and bismuth–tellurium have been determined. It is shown that compounds of these elements have a susceptibility value which cannot be deduced from the values of the constituents, and that in the susceptibility concentration curve the existence of a compound is most markedly shown. The curves are straight lines between the compounds and the single constituent when there is no miscibility. When there is miscibility the curves have rounded course. Complete diagrams are given of the cases investigated. J. F. S.

Magneton and Stere Numbers of Magnetic Cations. ADOLF HEYDWEILLER (*Ber. Deut. physikal. Ges.*, 1913, **15**, 821—825).—From investigations on the ion refraction of salts of manganese, iron, cobalt, nickel, copper, and chromium, the relationship between the stere numbers and the magneton numbers are compared, the latter values being taken from the measurements of Weiss (*Verh. Deut. Physikal. Ges.*, 1911, **13**, 736). It is shown that the stere number (p) of the bivalent cations are not very different, whilst those of the tervalent cations are also similar, but about 3/2 times as large as those of the bivalent cations. In all cases the stere numbers and magneton numbers (n) are of the same dimensions. In four cases, $p \gtrless n$, Cr''', Fe''', Ni'', and Cu'', in the case of Fe''' and Ni''' $p \triangleq n$, in three cases, Fe'', Mn'', and Co'' $p < n$. It is also shown that in those cases where there is approximately the same space-filling, the true ion volume is changed considerably when there is a change in the valency. The amount of the change is approximately in the ratio of the two valencies. J. F. S.

New Formulæ for Calculating the Cubic Expansion of Water. P. H. HOFBAUER (*Zeitsch. physikal. Chem.*, 1913, **84**. 762—763).—The author deduces two formulæ which give values for the cubical expansion of water that agree with the experimentally-determined values to the fifth decimal place. The first formula covers the temperature range 0—40°, and has the form

$$v = (e^{1/e} . r^{1/r})^{e(er . e^{1/e})}.$$

and the second covers the range 50—100°, and has the form

$$v = {}^{\log er}[(e^{1/e} . r^{1/r})^3].$$

in which r has the value $e\theta/277$, θ the absolute temperature of the water, v the corresponding volume, and e the base of natural logarithms. J. F. S.

Discontinuity of Temperature at the Limit of a Gas and an Absorbing Wall. K. LEONTIEV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, *Phys. Part*, 210—218).—The author has investigated, by von Smoluchovski's method (A., 1900, ii, 63), the manner in which the discontinuity of temperature of a gas at a glass wall depends on the temperature. The gases employed were ammonia, methylamine, ethylamine, methyl and ethyl chlorides, methyl bromide, and methyl ether, which undergo considerable adsorption at a glass surface.

The forms of the curves obtained for the relation between discontinuity and temperature may be explained on Lazarev's assumption (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 69) that the adsorption of the gas on the wall of the vessel influences the magnitude of the discontinuity. At low temperatures the gaseous lamina formed has a considerable effect, with the result that the conditions are excellent for the equalisation of temperature between the wall and the adjacent gas molecules; consequently, the extent of the temperature discontinuity diminishes. When the temperature is raised the adsorbed layer becomes lessened, and the discontinuity more marked; at a certain temperature of the wall the efficiency of the gaseous layer is determined solely by the general number of the molecules, and the conditions are then analogous to those prevailing with gases, such as air, which are only slightly adsorbed. Indeed, the curve for the discontinuity-coefficient in air possesses the same general form as the upper portions of the curves for the gases mentioned above.

That the variation of the discontinuity with temperature cannot be regarded as due exclusively to change of the coefficient of thermal conductivity is evident from the essentially different forms of the curves expressing the relations of these magnitudes to temperature.

T. H. P.

An Improved Method for the Determination of the Specific Heat and the Heat of Dilution of Liquids with Details in the Cases of Dilute Hydrochloric, Hydrobromic, Hydriodic, Nitric and Perchloric Acids, and Lithium, Sodium and Potassium Hydroxides. THEODORE W. RICHARDS and ALLAN W. ROWE (*Zeitsch. physikal. Chem.*, 1913, **84**, 585—610. Compare A., 1905, ii, 677; 1908, ii, 806).—The specific heats of the above-mentioned solutions have been determined by a modification of the method previously described (*loc. cit.*). It is shown that an uncertainty crept into the value of the determinations in previous experiments owing to undetermined temperature changes during the pouring of the alkali into the acid, and as the heat liberated in this reaction is the basis of the determination, the results were not as accurate as they might have been. The present experiments were carried out adiabatically in the usual manner, the liquid under investigation being placed in a platinum calorimeter. The acid which was to be neutralised was placed in a platinum vessel and sunk in the liquid in the calorimeter, and the alkali was contained in a smaller platinum vessel, which in its turn was sunk in the acid.

Both platinum vessels could be rotated, and so serve as stirrers. When the temperature of the whole system had become constant the vessel containing the alkali was opened at the bottom and the acid and alkali allowed to mix, and the heat thus generated, which was known exactly, used to heat up the surrounding liquid. The first experiments were carried out with water at a number of temperatures, and from them, assuming the specific heat of water had the value unity, the temperature-coefficient of the neutralisation of sulphuric acid by sodium hydroxide under the experimental conditions was −49·5 cal. per degree rise of temperature. The carefully prepared solutions of alkalis and acids were substituted for water and the specific heat determined. The results are shown to be correct to 0·0001. The following mean values are given for the temperature range 15·9—20·1°: $HCl,200H_2O$, 0·9814; $HCl,100H_2O$, 0·9634; $HBr,100H_2O$, 0·9433; $HI,100H_2O$, 0·9213; $HNO_3,100H_2O$, 0·9584; $HClO_4,100H_2O$, 0·9466; $KOH,100H_2O$, 0·9768; $NaOH,100H_2O$, 0·9664; $NaOH,200H_2O$, 0·9827; and $LiOH,100H_2O$, 0·9813. The molecular heats of the solutions are calculated, and it is shown that on dilution of $HCl,100H_2O$ to $HCl,200H_2O$ the added heat capacity of the gram-molecular weight is slightly less than the heat capacity of the added water; the same applies to the dilution of sodium hydroxide. From the molecular heats of the solutions of the type $MX,100H_2O$ it is shown that the value increases with increasing molecular weights for the halogen acids, and falls for the alkali hydroxides; perchloric acid has a somewhat larger value than nitric acid. J. F. S.

Specific Heat of Solids. HANS VON JÜPTNER (*Zeitsch. Elektrochem.*, 1913, **19**, 711—720).—A mathematical paper in which an expression is evolved, giving the relationship between specific heat and temperature for solid substances. The expression is applied to the known values for a number of substances. J. F. S.

Specific Heats of Some Binary Liquid Mixtures. ADOLFO CAMPETTI (*Atti R. Accad. Sci. Torino*, 1913, **48**, 968—977).—The binary mixtures of alcohol with diphenylamine, nitronaphthalene, α-naphthylamine, and salol have specific heats greater than those calculated from the law of mixtures (compare Schultze, A., 1912, ii, 624). Diphenylamine and α-naphthylamine show a rapid change of specific heat in passing from the solid to the liquid state, but the mixtures studied do not exhibit this behaviour. In the case of mixtures at a temperature below the m. p. of one component, this component has a specific heat corresponding with that which it would have in the superfused, not in the solid, state. R. V. S.

Cryoscopic Investigations of Solutions of Diethyl Ethylene Ether and Water. (Mlle.) V. A. UNKOVSKAJA (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1099—1108).—It was found by Makovecki that, with dilute solutions of diethyl ethylene ether in water, the lowering of the vapour pressure of the water is approximately twice as small as it should be according to Raoult's law. Since

Trouton's constant for this ether has the value 21·2, which is that given by non-associated liquids, the author has investigated the molecular freezing-point depressions of dilute aqueous solutions of diethyl ethylene ether.

It is found that, with increasing concentration of the ether, the molecular depression at first diminishes, but remains constant at a mean value of 18·63° for depressions lying between 0·3 and 1·6°. The initial diminution of the molecular depression is shown to be due to the supercooling influence of the bath. The results of this and a further series of measurements with solutions of higher concentration show that as the mol. % of the ether increases from 0·0506 to 15·18, the molecular depression of the freezing point diminishes only from 18·63 to 15·18. Hence, within the range of concentration investigated by the author, it seems impossible that the diminution of the vapour pressure of water by diethyl ethylene ether should be only one-half as great as that required by Raoult's law.

The molecular depressions for solutions of water in diethyl ethylene ether have also been investigated. On the assumption that the curves connecting the molecular depression with the logarithm of the concentration of the water give, throughout their whole course, a partial indication of the extent to which the water molecules are associated, it is seen that with increasing concentration association proceeds at first slowly and then rapidly; if the concentration is raised approximately to the cryohydrate point, association again slackens, and the curve becomes asymptotic to the log.-concentration axis. The greatest observed value for the molecular depression of the freezing point of diethyl ethylene ether is 41·4, and the mean value calculated from van't Hoff's formula, 39·05. Measurements of the specific heats of the liquid and solid ether gave the mean values 0·4203 and 0·2839 respectively.

T. H. P.

Synthesis of Natural Fats from the Point of View of the Phase Rule. II. The Ternary System: Tripalmitin–Stearic Acid–Palmitic Acid. ROBERT KREMANN and H. KLEIN (*Monatsh.*, 1913, **34**, 1291—1311. Compare A., 1912, ii, 1152).—A purely physical paper, forming the second of a series in which the freezing-point curves of systems approximating in composition to the mixtures of glycerides and fatty acids present in natural fats will be recorded and discussed. In the present paper tables and curves of the melting points of mixtures of the three substances mentioned in the title, taken two at a time, are first given, and then similar data are given for ternary systems in which two of the components are present in constant amount, with varying proportions of the third.

T. A. H.

Connexion between Boiling Point and Molecular Weight of Substances. J. C. THOMPSON (*Chem. News*, 1913, **108**, 189—191. Compare A., 1912, ii, 1136).—In an attempt to find a relationship between the boiling point and molecular weight of organic sub-

...nces, it has been found that the expression $T/\rho^{0.236}.M^{0.5}$ affords ... approximate constant for a large number of hydrocarbons. By ...eans of several examples it is shown, however, that the value of ...e function increases slightly as the proportion of double and ...ple bonds increases. An attempt is made to explain the observed ...fluence of unsaturation in terms of the attractive forces acting ...tween the carbon atoms. H. M. D.

New Formulæ for Calculating the Vapour Pressure of Water Vapour. P. H. HOFBAUER (*Zeitsch. physikal. Chem.*, 1913, **8...**, 764. Compare A., 1912, ii, 735; this vol., ii, 556).—In a ...evious paper the author deduces the formula

$$\log P/p = c \log \sqrt{\rho\delta . \rho'\delta'} + \log(1/\theta + 1/\Theta).$$

... the present paper the value of the constant c in the above ...pression is given, for the conditions $\Theta = 373°$ absolute, $P = 760$, ... the heat of evaporation, and δ the density at the normal boiling ...int, and $m = 0.434294$ as

$$c = \log(m . \Theta^2 dP/P . d\Theta) . \log\rho\delta.$$

...f this value is inserted in the above expression, the formula then ...kes the form:

$$P/p = e^{\Theta - \theta\sqrt{dP . dp/P . p . d\Theta d\delta}}.$$

J. F. S.

Vapour Pressure of Saturated Solutions. III. The Determination of the Vapour Pressure of Solutions of Sodium Chloride by the Boiling-point Method. ALEXANDER SPERANSKI (*Zeitsch. physikal. Chem.*, 1913, **84**, 160—188. Compare A., 1909, ..., 378; 1911, ii, 1065).—A continuation of previous work, in which ...e author had shown the expression $T \log_e p_0/p$ for concentrated ...lutions between 20° and 60° is a linear function of the tempera...ure; p_0 represents the vapour pressure of the pure solvent, and ... that of the solution at the temperature T. The present paper ...eals with the vapour pressure of sodium chloride solutions at ...igher temperatures. This was determined in a manostat in which ...e pressure could be kept constant to 1·5 mm. A full description ...f the apparatus is given. It is shown that for sodium chloride ...e value of $T \log_e p_0/p$ is not a linear function of the temperature, ...ut rises to a maximum at about 60° and then falls. It is shown ...at if the molecular weight of sodium chloride is calculated from ...e vapour-pressure determinations a value of 20·4 is obtained ...tween 30° and 100°, which indicates that sodium chloride disso...ates into 2·87 ions, that is, 58·5/20·4. This seems to point to the ...rmation of hydrates in the solution. J. F. S.

Determination of the Vapour Pressure of Saturated ...lutions by the Boiling-point Method. P. PAVLOVITSCH (*...eitsch. physikal. Chem.*, 1913, **84**, 169—178. Compare preceding ...stract).—The vapour-pressure curves of saturated aqueous ...lutions of copper sulphate, potassium nitrate, potassium chlorate,

and sodium sulphate have been determined, using the apparatus designed by Speranski (*loc. cit.*). It is shown that in the region 60—100° the vapour-pressure curve does not bend toward the temperature axis. The Bertrand formula $p=K(T-l)^{50}/T^{50}$ holds for saturated solutions of substances which have a solubility that changes but little with temperature. For solutions of salts the solubility of which changes rapidly with temperature, the formula holds if a suitable smaller index than 50 is chosen; the formula of Dupré-Hertz, however, holds even better. The formula of Speranski, $\log p=a\log C+b$, in which C is the concentration in grams per 100 grams of solvent, holds for solutions of copper sulphate and sodium sulphate, but not for potassium chlorate and nitrate. The value of $T\log_e p_0/p$ increases in a linear manner with the temperature for copper sulphate solutions; with sodium sulphate it increases in a less rapid manner; and with potassium chlorate and nitrate in a more rapid manner. The vapour-pressure curves of solutions of copper sulphate, sodium sulphate, and potassium chlorate are practically coincident, whilst that of potassium nitrate lies considerably beneath them. J. F. S.

Higher Valencies in Oxygenated Organic Compounds. I. Oxonium Compounds of Aliphatic Alcohols. Vladimir V. Tschelincev (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 841—864).—The author has measured the heat effects accompanying the formation of complexes of the three types PrOMgI,R·OH, PrOMgI,2R·OH, and PrOMgI,3R·OH, R representing methyl, ethyl, propyl, *iso*propyl, butyl, *iso*butyl, *sec.*-butyl, *tert.*-butyl, *iso*amyl, amyl (amylene hydrate), heptyl, or octyl.

The amounts of heat developed during the combination of successive molecules of the alcohol show that the formation of complex depends on the length and structure of the carbon atom chain of the alcohol radicle and on the position of the hydroxyl group. Union of 1 mol. of ethyl alcohol corresponds with a slightly larger development of heat than that of 1 mol. of methyl alcohol, but, in general, for primary, secondary, and tertiary alcohols, the heat effect diminishes in passing from methyl to ethyl to propyl; the diminution is then arrested, and the heat effect remains virtually constant as far as the octyl group.

The influence of the methyl group gradually weakens as its distance from the hydroxyl group increases. Thus, although the heat effects are greater for *iso*butyl than for *n*-butyl alcohol, with the amyl alcohols no such differences are observable.

The heat effects for secondary alcohols are sometimes greater and sometimes less than for primary alcohols. For tertiary alcohols the effects are generally less than for the primary or secondary alcohols; with *tert.*-amyl alcohols the higher valency of the oxygen is so weak that they give with the magnesium alkyl complexes only compounds containing 1 mol. of the alcohol.

These results may be compared with those of Ostwald's investigations of the dissociation constants of organic acids and of

denschutkin's measurements of the velocities of esterification of rganic acids (compare also Michael, A., 1909, ii, 219). T. H. P.

Higher Valencies in Oxygenated Organic Compounds. I Oxonium Compounds of Phenols. Vladimir V. Tschelincev *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 864—880).—Similar measure- ents have been made to those previously described (see preceding bstract), using, in place of the monohydric alcohols, phenol, *o*-, *m*-, nd *p*-cresols, thymol, carvacrol, *o*-, *m*-, and *p*-chlorophenols, bromophenol, *s*-trichloro- and tribromo-phenols, and *a*- and naphthols.

The results show that the position of the substituent in the enzene nucleus and, to a less degree, its character, exert a sub- tantial influence on the manifestation of increased valency by he oxygen of a hydroxyl group united to an aromatic ring.

Substitution by an alkyl radicle in the ortho-position of phenol owers the heat-effect of combination of the first complex molecule, nd, in the case of *o*-cresol, the development of heat by the reactions, $PrOMgI,C_6H_4Me\cdot OH + C_6H_4Me\cdot OH$ and $PrOMgI,2C_6H_4Me\cdot OH + C_6H_4Me\cdot OH$, is zero. When the substitution takes place in the neta-position, very slight lowering is produced in the heat-effect or each molecule of the phenol added. With para-substitution, the eat-effect is raised, lowered, and almost unchanged respectively or the first, second, and third molecule combined. With more omplicated substitution, as in thymol or carvacrol, the heat-effects re intermediate to those of *o*- and *m*-cresols.

When an acid radicle, such as chlorine, is introduced into the rtho-position in phenol, the amounts of heat developed on com- ination of the first and second molecules with the magnesium omplex are considerably diminished, and union with a third olecule does not take place. But if the acid substituent enters n the meta- or para-position, marked increases are observed in he heat-effects accompanying combination of the first two molecules, nd the heat-effects due to the third molecule are virtually nchanged and slightly raised with *m*- and *p*-chlorophenols respec- vely. Replacement of the chlorine in *p*-chlorophenol by bromine roduces but slight changes in the amounts of heat developed. nalogous results are obtained with two acid radicles in the two rtho-positions of phenol, either alone or with a third acid radicle n the para-position.

With the naphthols, the thermal changes are quite small in omparison with those obtained with phenol. Further, the higher alency of oxygen is, in general, manifested in weaker degree n aromatic compounds than in the corresponding aliphatic ompounds.

An alcohol, such as ethyl alcohol, which forms complexes with evelopment of considerable quantities of heat, displaces phenol rom its complexes almost completely.

Parallelism exists between the heats of formation of these com- lexes and the velocities of esterification, both with aliphatic lcohols and with phenols. T. H. P.

Exact Vapour Density Determinations of Some Liquid Organic Substances. ALFRED SCHULZE (*Physikal. Zeitsch.*, 1913, **14**, 922—926).—A modified Dumas method for the determination of vapour densities is described. The apparatus usually employed is modified by having a small bulb of about 5 c.c. capacity blown on to the bottom of the Dumas bulb. It is connected by means of a short capillary tube. In making a determination, the small bulb and about one-third of the large bulb are filled with the liquid under investigation. The whole is then placed in a thermostat until the last trace of liquid has disappeared, when it is sealed in the usual way. The apparatus is then removed from the thermostat and the small bulb dipped into liquid air, when the whole of the vapour is condensed in it. When this has happened, the small bulb is removed from the the larger by melting the capillary. The small bulb, on weighing, gives the weight of the vapour, and on filling the large bulb with water, the volume of the vapour is easily obtained. From determinations with a number of substances the author shows that the results obtained reach an accuracy of 99·7%. It is shown incidentally that carbon disulphide and nitrobenzene are associated to a small extent in the vaporous condition. J. F. S.

Compressibilities of Dilute Solutions of Certain Inorganic Salts. WILLIAM WATSON (*Proc. Roy. Soc. Edin.*, 1913, 33, 282—291. Compare A., 1911, ii, 793).—The compressibility of solutions of sodium carbonate, sodium hydroxide, potassium hydroxide, magnesium sulphate, and zinc sulphate have been determined in dilute solutions up to a pressure of 1000 atmospheres. The values of $\Delta K/C$ have been compared with those obtained by Tammann from the thermal expansion, where it is shown that there is a good agreement between the two. It is shown that a small molecular volume or a large contraction on solution is associated with a small compressibility of the solution. J. F. S.

The So-called Laws of Tate. THEODOR LOHNSTEIN (*Zeitsch. physikal. Chem.*, 1913, **84**, 410—418).—Polemical against Morgan's work on the weight of a falling drop, and the laws of Tate (A., 1911, ii, 372, 384, 584, 699, 857, 1064); see also Lohnstein (A., 1909, ii, 25). J. F. S.

The Weight of a Falling Drop and the Laws of Tate. XII. The Drop Weights of Certain Organic Liquids and the Surface Tensions and Capillary Constants Calculated from them. J. LIVINGSTON R. MORGAN and EDWARD C. STONE (*J. Amer. Chem. Soc.*, 1913, **35**, 1505—1523).—The drop weights, and hence the surface tensions and capillary constants, at various temperatures of the following organic liquids have been determined: methyl propyl ketone, paracetaldehyde, ethyl nitrate, nitromethane, butyl alcohol, *iso*butyl alcohol, allyl alcohol, formic, propionic, butyric, *iso*butyric, and *iso*valeric acids, *o*-toluidine, *p*-toluidine, formamide, dimethylnitrosamine, acetophenone, benzophenone,

ethyl propyl ether, acetal, furfuraldehyde, and anethole. Of these, only acetal, ethyl propyl ether, and *o*-toluidine were found to be non-associated.

In some cases the calculated critical temperature increased with the temperature of observation, the meaning of which is not obvious.

Benzophenone was investigated at temperatures as much as 39° below its melting point, but no abuormalities were observed in the supercooled liquid.

Ortho-compounds have a higher surface tension than para-compounds. T. S. P.

The Constants *a* and *b* of the van der Waals' Equation. PAUL FUCHS (*Zeitsch. physikal. Chem.*, 1913, **84**, 755—758. Compare Bose, A., 1909, ii, 989).—Bose (*loc. cit.*) puts forward the hypothesis that the attraction between molecules of equal mass will be greater the more complex the molecules. It is shown that this is not the case; for example, the *a* value for methane is 1·88, whereas that of ammonia is 4·10. It is also shown that in a series of gases containing an equal number of molecules the *a* value decreases with increasing molecular weight, whereas according to the Bose theory it ought to increase. The conclusion is drawn from the discussion of the values that the coustant *a* of the van der Waals' equation is not to be represented only by the force of the attraction between the molecules, that it is not absolutely constant, and that it is influenced by other conditions. J. F. S.

Total Surface Energy and Chemical Constitution. G. M. BENNETT and ALEC DUNCAN MITCHELL (*Zeitsch. physikal. Chem.*, 1913, **84**, 475—497).—A theoretical paper, in which it is shown that the total molecular surface energy in normal liquids is independent of the temperature, and that $(\gamma - t \,.\, d\gamma/dt)(Mv)^{2/3} = K$. This expression is shown to be an atomic function, $K = \Sigma(a)$. In associated liquids the value of K increases, but $(\gamma - t \,.\, d\gamma/dt)(Mxv)^{2/3} = K'$ should be constant, where x is the association factor of the liquid, and from this the value of K' can be calculated by the formula $x = (K'/K)^{3/2}$. J. F. S.

Viscosity and Surface Tension of Suspensions and Solutions of Muscular Proteins Under the Influence of Acids and Alkalis. FILIPPO BOTTAZZI and E. D'AGOSTINO (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 183—192).—The experiments relate to the product myosin (compare Bottazzi and Quagliariello, this vol., i, 1132), which yields with water a suspension which gradually passes into a solution when treated with acid or alkali. When potassium hydroxide is added, the viscosity rises in course of time to a maximum, and then decreases again. When a given suspension is treated with increasing amounts of potassium hydroxide or hydrochloric acid, the viscosity first attains to a maximum, and then diminishes. Lactic acid gives a similar result, but the maximum was not reached in the experiments quoted. If the viscosity of the suspension has already been augmented by the addition of lactic

acid, further addition of sodium chloride produces a considerable diminution in the viscosity of the liquid. The surface tension of the myosin suspension differs little from that of water, but the addition of acid or alkali causes a diminution of the surface tension of the solution. A solution of myoprotein (*loc. cit.*) has a low surface tension which is not much influenced by the addition of potassium hydroxide, but is diminished by addition of hydrochloric acid, protein being simultaneously precipitated. R. V. S.

Internal Friction of Liquids. ALEXIUS J. BATSCHINSKI (*Ann. Soc. d'Encour. Sci. Exp., Suppl.* 3, 1913, *Reprint*, 1—68).—Since with gases the internal friction is conditioned principally by the transference of motion as a result of molecular impacts, whilst in the case of liquids it is due to the action of molecular forces, the viscosity of liquids must differ essentially from that of gases. Unsuccessful attempts have been made by various investigators to express analytically the dependence of the viscosity of liquids on the temperature, and it would seem probable that such viscosity can be expressed more simply as a function of the specific volume. With the single exception of water, the viscosity is a diminishing function of the specific volume, and the author deduces the expression $\eta = c/(v-\omega)$, where v represents the specific volume, and c and ω are constants characteristic of any particular liquid. Hence the curves connecting the fluidity, $1/\eta$, and the specific volume should be rectilinear. Such curves have been constructed for a series of eighty-seven substances investigated by Thorpe and Rodger (*Phil. Trans.*, 1894, **185**, *A*, 574), for mercury and carbon dioxide; also for ether, ethyl acetate, and benzene at temperatures higher than the ordinary boiling points.

It is found that the law $\eta = c/(v-\omega)$ holds for all non-associated liquids over wide limits of variation of the co-ordinates; with ethyl acetate, for example, over a temperature-interval exceeding 180°. This law is not obeyed by associated liquids, but in the case of very dense gases it seems to be applicable to the same extent as with liquids. With sixty-six of the liquids the values of c and ω have been calculated, and the values of η then obtained from the above formula compared with the observed values; the differences are mostly very small, and only in rare cases exceed 1%.

That the law holds also when η and v undergo alteration as a result of change of pressure is shown for carbon dioxide, ether, and benzene. From the formula $\eta = c/(v-\omega)$ is derived $\omega/v_1 + \beta/\alpha = 1$, where v_1 is the specific volume of the liquid at a pressure of one atmosphere, β is the coefficient of compressibility, and $\alpha = 1/\eta \, . \, d\eta/dp$.

The constant ω may be defined as the specific volume corresponding with infinitely great viscosity of the liquid. It is hence termed the "limiting volume," and $v-\omega$ the "free volume." The value of ω is found to be intermediate to those of the liquid and solid at the solidifying temperature. The constant c may be regarded as the value of the viscosity coefficient for a free volume of 1.

When the free volume is relatively very small, marked divergence

from the law $\eta = c(v - \omega)$ appear, so that the law loses in accuracy when the molecules approach one another too closely.

For all substances which obey the law, the limiting volume, ω, equals approximately 0·307 times the critical volume, and is very nearly the parameter b of van der Waals' equation.

The molecular limiting volume, $M\omega$, is additive in character. The increments, ϵ, of this magnitude have been calculated for the separate elements in a compound and, in fifty-three out of sixty-six cases, the observed values of $M\omega$ and those calculated from the increments differ by less than 2%.

Consideration of the dependency of the constant c on the critical constants or on the parameters of van der Waals' equation leads to the conclusion that c is proportional to the square root of the specific molecular attraction, a. The relation between the author's law and the viscosity formulæ of other authors is discussed.

T. H. P.

Internal Pressure of Liquids. ALBERT P. MATHEWS (*J. Physical Chem.*, 1913, **17**, 603—628. Compare this vol., ii, 300, 494).—A number of methods are described which have been employed in the computation of the internal pressure of liquids. In these methods the value of "a" of the van der Waals' equation is derived respectively: (1) from the surface tension, on the assumption that the thickness of the surface layer is $T_c/(T_c - T)^{2/3}$ molecular diameters; (2) from Eötvös's law by a modification of Young's method; (3) from van der Waals' equation as applied to the critical temperature, the assumption being made that $b_c = 2V_c/S$, where S is the critical coefficient, and is given by $S = RT_c/V_cP_c$; (4) from the internal heat of vaporisation at temperatures in the neighbourhood of the critical temperature; and (5) from the molecular weight M and the number of valencies N by means of the formula $a = 1{\cdot}259 \times 10^{11} . (MN)^{2/3}$ (compare previous papers, *loc. cit.*).

All five methods give practically the same results, but the values are uniformly higher than those obtained previously, with the exception of Lewis's values calculated from the latent heat of expansion. The data for pentane and ethyl ether are also found to afford values for the internal pressure, which remain constant over a wide range of temperature. This seems to show that in the absence of association, the molecular cohesion is independent of the temperature.

H. M. D.

Pressure of Flow and Hardness of Plastic Substances. NIKOLAI S. KURNAKOV and SERGEI F. SCHEMTSCHUSHNI (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1004—1076).—The authors first give a summary of previous work on the hardness and pressure of flow of plastic substances, which behave like liquids of high internal friction under slow deformation, and like elastic, brittle solids under rapid deformation. They have devised a special apparatus for measuring the pressure of flow for such substances, and have applied it to the investigation of a large number of them.

Under constant conditions, the curves representing the pressures

on the piston of the vessel from which flow takes place as ordinates and the times as abscissæ are of four principal types: (1) After an initial period of increase, the pressure reaches a limit, and then remains constant as the flow continues. (2) The pressure first increases, then diminishes, and finally remains constant; in a particular form of this type, the initial increase is followed by continuous increase during the period (0·5—6 hours) of the observation. (3) The rising curve exhibits a bend corresponding with the initial pressure of flow; the establishment of flow lies outside the limits of pressure measured by the apparatus. Such diagrams are obtained with metals. (4) With this type, characteristic of substances brittle under the experimental conditions, the curve first rises rapidly, and then assumes a sharp zigzag form, indicating sudden rises and falls in the pressure within the vessel. A diagram of this kind is given by the double compound of silver chloride and thiocarbamide, $AgCl,2CS(NH_2)_2$. Many intermediate forms of diagram exist to these four types.

At constant temperature the pressure of flow for all types of diagram increases with the velocity of deformation. The latter increases more slowly than the pressure.

The phenomenon of relaxation or diminution of the pressure while the flow remains constant (see type 2, above) is considered analytically, and it is shown that investigation of the diagram of flow affords a general mechanical method for measuring the time of relaxation, which is a fundamental magnitude in establishing the different conditions of solids. The time of relaxation, T, is, indeed, a measure of the brittleness, whilst its reciprocal, $1/T = k$, represents the characteristic of plasticity. With constant rate of flow, the pressure of flow is proportional to the coefficient of viscosity.

Results are given of the investigation of the flow of a large number of elements, salts, and organic compounds, some of the conclusions drawn from these being as follows. In general, the accumulation of oxygen in a molecule, for example, by the conversion of potassium iodide into iodate or of potassium or silver nitrite into nitrate, increases the pressure of flow and favours brittleness. Among organic compounds, marked plasticity and low pressures of flow are observed with derivatives of the terpene group, for instance, camphene, camphor, pinene hydrochloride, borneol, and menthol.

The data obtained with binary systems show that: (1) The formation of solid solutions and isomorphous mixtures is accompanied by increase in the hardness and pressure of flow. (2) The variation of the hardness of a continuous series of solid solutions is expressed by a continuous curve exhibiting a maximum. (3) The hardness of systems formed by the mechanical superposition of the components is a linear function of the composition. (4) The formation of solid solutions of plastic substances is accompanied by increase in the temperature-coefficient of hardness (or viscosity). (5) For metallic alloys, the diagrams of hardness and its temperature-coefficient in relation to the composition possess the

inverse or antibatic (compare Luther, *Zeitsch. Elektrochem.*, 1906, 12, 97) forms of those of the corresponding diagrams of electrical conductivity and of the temperature-coefficient of electrical resistance.

It is shown that the hardness number and the pressure of flow may serve as characteristics of the purity of metals. Increase of the hardness and of the viscosity coefficient of solid solutions possessing maximum hardness is not merely dependent on increase of the modulus of elasticity E in the equation, $\eta = ET$, but is also related to increase in the time of relaxation T. This conclusion is confirmed by the results obtained with an extensive series of solid solutions of copper and iron (brass, bronze, steel, etc.) of wide industrial application. Thus, tempered steel, distinguished by its great hardness, possesses a lower modulus of elasticity than soft iron. Since the time of relaxation may be taken as a measure of brittleness, it follows that increase in the hardness of solid solutions due to increased time of relaxation should be accompanied by increased brittleness. Such a conclusion receives complete experimental confirmation. Of great technical interest are metallic solid solutions, the increased hardness of which is conditioned chiefly by increase in the modulus of elasticity; such substances, which should be hard without greatly augmented brittleness, are to be investigated later.

In many cases in which the formation of definite chemical compounds is accompanied by loss of internal energy from the reacting substances, increase in the hardness occurs, in some instances to that of the hardest component. Contrary to what is observed with solid solutions, the increased hardness and pressure of flow with definite compounds formed with considerable development of heat depends on simultaneous increase of the times of relaxation and of the moduli of elasticity of the components. Comparison of the moduli of elasticity serves as a new means of distinguishing solid solutions from chemical compounds, since, with a substance of the former class, the modulus of elasticity is either equal to or less than the arithmetic mean of those of the components.

T. H. P.

Variation of the Resilience of Some Industrial Alloys of Copper as a Function of the Temperature. LÉON GUILLET and VICTOR BERNARD (*Compt. rend.*, 1913, **157**, 548—550. Compare this vol., ii, 710).—A study of the variation in resilience with temperature of some seven bronzes containing from 3·5 to 20% of tin and varying proportions of lead and zinc, four brasses, and one aluminium bronze. The results are expressed by curves giving the breaking strain in kilograms/sq. cm., and show that lead acts unfavourably as regards resilience. The aluminium bronze shows rapid decrease in resilience with rise in temperature. W. G.

Weight Relations Occurring when Liquids are Imbibed by Absorbent Paper. I. P. KRAIS (*Zeitsch. angew. Chem.*, 1913, 26, 598—600).—Strips of dry filter paper were arranged so that

the bottom part was immersed in a given liquid. After a given time sections of the filter paper above the surface of the liquid were cut out, and the amount of liquid absorbed by them was determined by weighing. It was found that the amount of liquid absorbed diminished as the height above the surface of the liquid increased.

The experiments are only preliminary, since great difficulties have been experienced in obtaining filter paper uniform in quality, and in determining the exact conditions under which comparative experiments can be made. T. S. P.

Dissociation of Mercuric Oxide. GUY B. TAYLOR and GEORGE A. HULETT (*J. Physical Chem.*, 1913, **17**, 565—591).—The dissociation pressure of mercuric oxide has been measured at temperatures between 360° and 480° by static and dynamic methods. The rate of decomposition of the oxide is very slow, but the equilibrium pressures can be attained in presence of suitable catalysts. The decomposition is accelerated by finely divided platinum, ferric oxide, manganese dioxide, and cadmium oxide, whilst aluminium and stannic oxides are without effect. The total dissociation pressure amounts to 90 mm. at 360°, 141 mm. at 380°, 231 mm. at 400°, 387 mm. at 420°, 642 mm. at 440°, 1017 mm. at 460°, and 1581 mm. at 480°. From these numbers the heat of dissociation of the oxide is calculated to be 76,400 cal., which is in good agreement with the calorimetric data.

From the variation of the dissociation pressure with the temperature it is shown that mercuric oxide is stable in the air at the ordinary temperature in presence of mercury, and that this is the case even under greatly reduced partial pressure of oxygen. The data show further that mercury may oxidise under ordinary atmospheric conditions; the rate is very small, but may be greatly accelerated by catalysts.

Measurements have also been made with the yellow oxide, and these show that the dissociation pressure curve is identical with that of the red oxide, indicating that these do not represent different modifications of the oxide. H. M. D.

Examination of Dolezalek's Gas Solubility Theory with Radium Emanation. RICHARD SWINNE (*Zeitsch. physikal. Chem.*, 1913, **84**, 348—352).—The Dolezalek theory of gaseous solubility (A., 1910, ii, 184) has been examined for several liquids with radium emanation. It is shown that for normal liquids the theory holds approximately. With strongly associated liquids a great divergence is observed between the molecular weights thus deduced and that obtained by the more usual methods. J. F. S.

Solubility Differences on Crystal Surfaces. HANS KUESSNER (*Zeitsch. physikal. Chem.*, 1913, **84**, 313—320).—A theoretical paper in which the solubility and surface tension on crystal faces are considered. The conditions which must be fulfilled for equilibrium with a crystal possessing both cubic and octahedral faces are mathematically deduced. J. F. S.

Liquid Crystals of Ammonium Oleate. OTTO LEHMANN (*Zeitsch. Kryst. Min.*, 1913, **52**, 592—601).—A reply to Mlodziejovski (this vol., ii, 306). L. J. S.

New Theory of Allotropy. ANDREAS SMITS (*Zeitsch. physikal. Chem.*, 1913, **84**, 250—256).—Polemical, an answer to Tammann's criticism (this vol., ii, 193, 679) of the author's previous papers on the theory of allotropy (A., 1910, ii, 195, 400; this vol., ii, 393). J. F. S.

A New Theory of Allotropy. II. GUSTAV TAMMANN (*Zeitsch. physikal. Chem.*, 1913, **84**, 753—754).—Polemical. A reply to Smit's answer (preceding abstract) to the author's previous criticism (this vol., ii, 679). J. F. S.

Ostwald's Law of Transition by Steps in the Light of the Theory of Allotropy. ANDREAS SMITS (*Zeitsch. physikal. Chem.*, 1913, **84**, 385—409. Compare Ostwald, A., 1897, ii, 308).—The author shows that the theory of allotropy (A., 1910, ii, 400) leads to the following conclusions: (1) On suddenly cooling the vapour of a stable modification of a substance, separation takes place of a liquid or of that solid form which corresponds most nearly in its composition with the vapour. (2) Sudden precipitation of an allotropic substance from a solution gives rise to that form which corresponds with the equilibrium conditions of the solution. If this equilibrium lies strongly to the side of the pseudo-component which prevails in the metastable modification, then the precipitated solid substance will be transformed into the metastable modification. A new hypothesis is put forward to cover the phenomena which occur during slow operations, namely, that every phase is operative in part in the formation of a new phase. The theory of allotropy coupled with the new hypothesis leads to the following conclusions: (1) When the composition of the different modifications of a substance are widely dissimilar, then that modification which has a composition most nearly like that of the liquid phase will separate from the supercooled system. The same applies to the separation of new phases from the vapour phase. (2) In those cases where the various modifications have similar compositions irregularities are likely to occur. (3) The spontaneous crystallisation of the stable or metastable form of a substance from a supersaturated solution depends entirely on the internal equilibrium of the solution. J. F. S.

Relationship of Unstable Forms to Stable Forms. HERMANN LAUTZ (*Zeitsch. physikal. Chem.*, 1913, **84**, 611—641).—The relationships between the stable and unstable forms of a number of substances are studied. Resorcinol is shown to exist in two stable and two unstable forms. At 70·8° the stable form II passes into the stable form I. These have specific volumes at 20°: I, 0·774; II, 0·787. The linear crystallisation velocity of the two stable forms is determined and shown to be about the same as

that of the unstable form III: 0·8 mm.—1·0 mm. per minute. The two crystalline forms and the amorphous form are examined, and the linear crystallisation velocity is determined for the pure substances and for mixtures of these substances and phthalide. Similar velocity determinations are carried out for the two forms of phthalide with addition of triphenylguanidine. Experiments are described on the transition of the stable form of tristearin into the unstable form, as well as on the crystallisation velocity. The relationships between the unstable forms of the following binary mixtures are studied: Acetamide–triphenylguanidine, acetamide–phthalide, triphenylguanidine–triphenylmethane, and triphenylguanidine–phthalide. J. F. S.

Method for the Determination of the Size of Colloidal Particles. A. V. Dumanski (*Kolloid. Zeitsch.*, 1913, **13**, 222—223). —A correction. The formula of Einstein, which was employed by the author in computing the density of colloidal particles (this vol., ii, 194) has now been replaced by Einstein's more exact formula, and corrected numbers representing the density of the colloidal particles of arsenious sulphide are recorded. H. M. D.

Precipitation of Colloids. III. Karl Spiro (*Biochem. Zeitsch.*, 1913, **56**, 11—16).—The H' concentration of mixtures of solutions of various salts with egg-white solutions was determined colorimetrically and electrometrically. The H' of such mixtures was calculated on the assumptions that the product (H).(OH) = constant = K_w, and that in mixtures of solutions containing only completely dissociated electrolytes, the difference between the sum of the total H and total (OH) ions does not change. The numbers experimentally found differed from the calculated numbers. In the majority of cases, the numbers found for p_H approximated more to the p_H of the protein solution. In the case of acetates and fluorides, the p_H numbers found approximated more to those of the salts. S. B. S.

A Neutral Oil Emulsion as a Model of a Suspension Colloid. Ridsdale Ellis (*Trans. Faraday Soc.*, 1913, 9, 14—25).—The effect of acids and alkalis on the interface potential of an oil emulsion (A., 1912, ii, 13) has been determined. A strong maximum is found in neutral or faintly alkaline solutions. These emulsions have the advantage over other colloids of not undergoing coagulation. The effect on stability has been determined approximately by experiments with a simplified form of nephelometer. Maximum stability is found in a $N/1000$-alkali solution. The surface tension of the oil is very little affected by acids or alkalis. The concentrations of salts with ter-, bi-, and uni-valent cations required to neutralise the charge on the globules are in geometrical ratio. The results are in accordance with the hypothesis of an electrical double layer around the particles. With colloidal ferric hydroxide, the oil globules first become coated with a solid or semi-solid layer, which prevents coalescence of the globules, and

then coagulation occurs by the adhesion of the hydroxide precipitate. These phenomena have been observed microscopically.

C. H. D.

New Experiments on Colloids. T. A. COWARD (*Trans. Faraday Soc.*, 1913, 9, 142—154).—Experiments with a solution of casein, pepsin and hydrochloric acid show that the enzyme is greatly checked, without being destroyed, by dilution. Further experiments with hydrosols of gold, gamboge, mastic and arsenious sulphide show that the number of submicrons per unit volume may even be reduced when the concentration of the hydrosol is increased. Both negative and positive sols show at one stage of dilution a departure from the usual course of increasing submicrons with increasing dilution. This stage is assumed to be that of electrical neutrality.

Cataphoretic measurements show an increase of submicrons with increased acidity of the dispersion medium; at the same time the velocity of the submicrons increases to a maximum. The charge is not reversed in sign at the acid coagulation point. C. H. D.

The Condition Diagram of Water. GUSTAV TAMMANN (*Zeitsch. physikal. Chem.*, 1913, 84, 257—292).—The author constructs a diagram of condition for water from the results of his previous experiments (A., 1910, ii, 495), which are compared with those of Bridgman (this vol., ii, 39). The transformations of the various forms of ice into one another are discussed, and the general relationships under pressures of 2000—2500 kilos. From a study of the ζ surface, it is shown that four forms of ice of group I, one form of group II, and two forms of group III exist. J. F. S.

Relationship of the Volume Surface and Polymorphism of Water. GUSTAV TAMMANN (*Zeitsch. physikal. Chem.*, 1913, 84, 293—313. Compare preceding abstract).—The determinations of Amagat on the volume surface of water appeared to show that above pressures of 3000 kilos., water would behave as a normal liquid. The researches of Bridgman have shown, however, that as the pressure is increased to 20,000 kilos., the abnormalities increase, and that consequently the view deduced from Amagat's work is incorrect. The present paper is a mathematical examination into the connexion between the abnormalities of the volume surface and the polymorphism of water. It is shown that evidence is obtainable of six molecular groupings on the volume surface, and that five modifications of ice are known. The sixth molecular grouping can only crystallise under very high pressure and at relatively high temperature. J. F. S.

The Change $S_{rh} \rightarrow S_{mon}$. HUGO R. KRUYT (*Zeitsch. physikal. Chem.*, 1913, 84, 498—500).—Polemical. An answer to Nernst's criticism (this vol., ii, 668) of the author's paper (this vol., ii, 132).

J. F. S.

Equilibria in the System $MgCl_2$–NH_3–H_2O. D. E. DIONISIEV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 905—912).—Loven's investigations (A., 1896, ii, 413) showed that, in systems containing a magnesium salt, ammonia, and water, no double or complex magnesium salt is formed, and that the concentrations of the reacting molecules are subject to the law of mass action. When ammonia acts on a magnesium salt, the magnesium hydroxide formed is not wholly precipitated, but remains partly in solution, the dissociated portion being in equilibrium with the non-dissociated. Loven's data refer to the region of increasing precipitate, and the author has now investigated the equilibria also in the region of diminishing precipitate.

The results show that, in the region of increasing precipitate, gradual increase in the concentration of the ammonia is accompanied by gradual increase of the ammonia-content of the liquid phase, whilst the quantity of magnesium constantly diminishes. In the region of diminishing precipitate, similar results are obtained with the exception that the concentration of the magnesium in the liquid phase shows continuous increase; when, however, the ammonia reaches a certain concentration, the magnesium- and ammonia-contents of the liquid phase undergo, firstly, a sudden increase, and then a decrease. This behaviour seems to be due to the separation of a product of variable composition (compare Kurilov, A., 1906, ii, 349). T. H. P.

Equilibria in Systems Composed of Copper Nitrate, Ammonia and Water. NIKOLAUS V. STASEVITSCH (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 912—930).—In the region of increasing precipitate, the composition of the precipitate formed by this system varies with the concentration from $2·79Cu(OH)_2,Cu(NO_3)_2$ to $2·97Cu(OH)_2,Cu(NO_3)_2$. The divergence of these compositions from $3Cu(OH)_2,Cu(NO_3)_2$ or $Cu(OH)_2,Cu(OH)NO_3$ may be due to experimental error, so that the composition may correspond with that of the zinc compounds obtained under similar conditions (A., 1911, ii, 476). This solid phase must be classed with products of combination of the first group (compare Kurilov, A., 1911, ii, 873). As regards the liquid phase, the concentration of the NH_4 ions here increases parallel with that of the ammonia added, the latter being almost completely converted into ammonium nitrate; the copper nitrate, being a salt of a weak base, undergoes hydrolysis, and leads to the formation of the product of combination mentioned above.

In the region of diminishing precipitate, the composition of the solid phase is characterised by the following values for the coefficient of the cupric hydroxide: 2·88, 2·89, 9·38, 114·63, 219·82, 90·33, 49·55, 31·20, 44·42, 41·24. The liquid phase is characterised by a rapid rise in the free ammonia, as was found with salts of zinc (*loc. cit.*), but the same is not the case with the nitric acid and the ammonia.

The phenomena in the region of discontinuity were found to depend on the concentration, temperature, and time. In the solid

phase blackening occurs, just as was observed by van Bemmelen ("Die Absorption," 180) in his experiments with cupric hydroxide obtained from copper sulphate and alkali hydroxide.

Investigations were also made of the electrical resistance and electromotive force of the systems, which were likewise submitted to ultramicroscopical examination. T. H. P.

The Nature of the Process which Occurs in the Partition of a Substance between Two Solvents. GEORG VON GEORGIEVICS (*Zeitsch. physikal. Chem.*, 1913, **84**, 353—364).—The partition coefficient law and the Boedecker modification of it are theoretically considered. It is shown that whilst the x value less than unity in the Boedecker formula can be explained by a dissociation of associated molecules, it is impossible to find an explanation for those cases in which x is greater than unity. The author shows that if the partition of a substance between two solvents is strictly dependent on the molecular size of the dissolved substance, then the x value of the partition formula must run parallel with the association factor for the freezing-point determinations. This is shown in the case of formic acid and butyric acid in water and benzene not to be in accordance with fact. Consequently the conclusion is drawn that the partition law cannot be applied to all solutions any more than it can to the partition of a substance between a liquid and a solid. It is shown that there is no real difference between the two processes, and consequently some cases of abnormal partition must be explainable on the assumption that an adsorption in addition to a solution has taken place. The similarity between adsorption by solid substances and cases of abnormal partition is pointed out, and possible results which may accrue should a liquid absorption in these cases be investigated. J. F. S.

The Combustion of Gaseous Mixtures and the Ignition Temperatures. J. TAFFANEL and LE FLOCH (*Compt. rend.*, 1913, **157**, 469—471. Compare this vol., ii, 574).—A study of the ignition temperatures of several gases, namely, methane, hydrogen, carbon monoxide, acetylene, ethylene, pentane, and finely divided oil, in varying proportions with air. The mixture is suddenly introduced into a vessel the walls of which are at a definite temperature, and the time of ignition recorded by a manometer. The effect of varying the size of the vessel is also given. The ignition temperature is a relative value depending on the conditions of ignition. The retardation of ignition (compare *loc. cit.*) is a general property, and not particular to methane. W. G.

Rôle of the Solvent in Chemical Kinetics. II. HANS VON HALBAN (*Zeitsch. physikal. Chem.*, 1913, **84**, 129—159. Compare A., 1909, ii, 722).—The solubility of p-nitrobenzyl chloride has been determined in twenty-six solvents, and the following gram-molecular concentrations per litre found: methyl alcohol, 0·39; ethyl alcohol, 0·31; propyl alcohol, 0·25; amyl alcohol, 0·20; butyl alcohol, 1·12;

acetic acid, 0·97; acetone, 3·02; acetophenone, 2·54; paracetaldehyde, 1·23; ether, 0·85; acetonitrile, 2·87; nitromethane, 2·87; *o*-nitrotoluene, 2·40; nitrobenzene, 2·66; ethyl acetate, 2·19; ethyl benzoate, 1·98; ethyl nitrate, 2·31; *iso*amyl bromide, 0·66; bromobenzene, 2·50; chloroform, 2·70; carbon tetrachloride, 0·52; benzyl chloride, 1·99; *a*-bromonaphthalene, 2·03; *n*-hexane, 0·049; *iso*pentane, 0·028; and benzene, 2·14. The solubility of trimethylamine was determined in methyl alcohol, propyl alcohol, ethyl alcohol, amyl alcohol, benzyl alcohol, acetone, acetophenone, ether, acetonitrile, nitromethane, *o*-nitrotoluene, nitrobenzene, ethyl acetate, ethyl benzoate, chloroform, *a*-bromonaphthalene, hexane, and benzene. The solubility of triethylamine was determined in hexane and nitromethane. The vapour-pressure curves of mixtures of ethyl iodide and *n*-hexane, and of ethyl iodide and nitromethane, were determined, and both shewn to exhibit maxima. The velocity of reaction between *p*-nitrobenzyl chloride and trimethylamine was determined in the same sixteen solvents in which the solubility of trimethylamine was determined. In every case the reaction is of the second order, and the influence of the solvent is generally of the same nature as that found by Menschutkin and Walden for the reaction between ethyl iodide and triethylamine (A., 1908, ii, 159). It is shown that the product of the solubilities of *p*-nitrobenzyl chloride and trimethylamine in different solvents varied but slightly with the solvent. Consequently the van't Hoff constants, made up of the product of the solubilities of the two reacting substances and their velocity constant, varied in the same way as the velocity constants. It is therefore not possible to explain the influence of the solvent on the velocity constant in these cases to a shifting of the equilibrium conditions. This is seen more markedly when the variations of the van't Hoff constant are considered alongside the variations of the velocity constant: the former can be represented by 400,000, whilst the latter are represented by 9300. The results are discussed, and it is shown that it is not possible to state generally that the influence of the solvent on the velocity constant is due to a shifting of the equilibrium conditions, but that a catalytic action of the solvent must be assumed to take place in many cases. J. F. S.

Kinetics of Reactions of Ester Formation. VIII. EGOR I. ORLOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 706—740. Compare this vol., ii, 681, 682, 683).—According to Kistiakovski (A., 1899, ii, 13), the reaction velocity for the formation of ethyl formate in aqueous ethyl alcohol is expressed by the equation, $dx/dt = k(A-x) - k_1x$. Calculations in accordance with the considerations advanced by the author show that the results are in good agreement with the general formula: $dx/dt = k(A - mx)$.

Further, in order to calculate the velocity constants of ester formation in methyl alcohol, it is unnecessary to make use of the complex empirical equations suggested by Goldschmidt and Thuesen (A., 1912, ii, 1154). When the esterification takes place in absence of water, the results obtained by these authors are in good agree-

ment with the formula $dx/dt = k(A - mx)$, whilst when water is present, the course of the esterification follows the more complete equation deduced by the author (*loc. cit.*).

An ionic theory of esterification is developed, according to which charges are communicated to the alcohol molecules from the ions of the catalyst and of the organic acid. This theory completely explains the processes of ester-formation, and is in agreement with the experimental data and with the law of mass action.

T. H. P.

The Decomposition of Chloroacetic Acid. HANS VON EULER and HENRY CASSEL (*Zeitsch. physikal. Chem.*, 1913, **84**, 371—379).—It is shown that the reaction:

$$Cl{\cdot}CH_2{\cdot}CO_2H + H_2O = HCl + OH{\cdot}CH_2{\cdot}CO_2H,$$

is influenced very strongly by ultra-violet light of short wave-length. A series of experiments on the velocity of this reaction have therefore been effected in the dark, and in the light of a quartz mercury lamp. It is shown that just as in the experiments carried out in the dark the amount of decomposition is not quite proportional to the time of exposure to the light, but that the reaction constant decreases with the time of exposure. This is due to the retarding influence of the acid formed in the reaction. In the dark experiments the reaction constant is practically independent of the concentration of the chloroacetic acid, whilst in the illuminated experiments the constant decreases with increase in the concentration. The reaction constant at 27·5° is $10^6k = 38{\cdot}0$, which implies that the light has increased the velocity of the reaction 50 times. Bromoacetic acid is shown to be much less sensitive to light than chloroacetic acid, the reaction constant being about three times as large in the latter case as in the former for a normal solution.

J. F. S.

Catalysis of Hydrazine by Platinum Black. ALEXANDER GUTBIER and K. NEUNDLINGER (*Zeitsch. physikal. Chem.*, 1913, **84**, 203—249).—The catalysis of hydrazine hydrate by platinum black and the influence of the presence of ammonia, barium hydroxide, and sodium hydroxide has been studied. It is shown that the results of Tanatar (A., 1902, ii, 386, 495) and Purgotti and Zanichelli (A., 1904, ii, 329) do not strictly represent the course of the decomposition, but that those of Tanatar under special conditions will be correct. Hydrazine is catalysed by platinum black according to the equation $3N_2H_4 \longrightarrow 4NH_3 + N_2$, and there is no evidence of the formation of hydrogen or nitrous oxide. The attempt to determine the order of the reaction led to indefinite results, from which the conclusion was drawn that a heterogeneous catalysis occurred. The platinum black, although prepared by the same process, showed widely differing catalytic activity. The constants calculated for the second and third order reactions decreased rapidly as the reaction proceeded, and this is attributed to the retarding action of the ammonia as it is formed, although the addition of ammonia previous to the reaction had not this effect.

In the presence of barium hydroxide the catalysis followed different lines, and the liberated gas contained hydrogen; if the relationship of barium hydroxide and hydrazine was equimolecular, 50 per cent. of the evolved gas was hydrogen, and these conditions represent the case from which Tanatar deduced the reaction $2N_2H_4 \longrightarrow 2NH_3 + N_2 + H_2$ for the catalysis of hydrazine. The maximum percentage of hydrogen in the evolved gas is 66·6%, and this is obtained when the concentration of the barium hydroxide is infinitely large. This corresponds with a decomposition $N_2H_4 = N_2 + 2H_2$. The decomposition of hydrazine in the presence of barium hydroxide is represented by the equations below, in which x is the number of molecules of barium hydroxide present when one molecule of hydrazine is employed: $3N_2H_4 \longrightarrow 4NH_3 + N_2$; $xN_2H_4 = xN_2 + 2xH_2$; $(3+x)N_2H_4 = 4NH_3 + (1+x)N_2 + 2xH_2$.

Barium hydroxide, in addition to changing the direction of the decomposition, also retards it. Sodium hydroxide has the same influence as barium hydroxide, except that double the quantity is required. The action of the two hydroxides is attributed to the driving back of the dissociation of hydrazine hydrate, which indicates that it is the undissociated hydrazine which breaks up into hydrogen and nitrogen. The mechanism of the decomposition is shown to be as follows: The hydrazine breaks up into hydrogen and nitrogen in the presence of platinum black; the nascent hydrogen then reduces two molecules of hydrazine to ammonia. Should, however, the dissociation of the hydrazine hydrate be prevented by the presence of strong bases, the reducing action of the nascent hydrogen is retarded, and consequently free hydrogen is liberated. The velocity of the decomposition of hydrazine is proportional to the quantity of the catalyst present, and is uninfluenced by glass. The hydrazine can only be decomposed to the extent of 93%. The order of reaction could not be determined, but is shown to depend on the condition of the platinum black.

J. F. S.

Action of Neutral Salts in the Catalysis of Esters. HUGH S. TAYLOR (*Medd. K. Vetenskapsakad. Nobelinst.* 2, No. 34, 1—20).—The influence of potassium chloride on the catalytic activity of hydrochloric acid has been examined in a series of experiments on the hydrolysis of methyl acetate, ethyl acetate, propyl acetate, ethyl propionate, ethylene diacetate, and triacetin.

The observations were made at 25°, the concentration of the acid being 0·1 molar, and that of the neutral salt 1 molar. The influence of the neutral salt is expressed in terms of Δ, where $\Delta = 100(K_2 - K_1 \cdot \alpha_2/\alpha_1)/K_1 \cdot \alpha_2/\alpha_1$, K_1 and K_2 being the velocity constants without and in presence of neutral salt respectively, α_1 and α_2 the corresponding degrees of ionisation of the acid.

Although the results seem to show a slight increase in salt effect with increasing complexity of the ester, it is probable that the variation from the mean value of $\Delta = 45$ is within the limits of experimental error. This leads to the conclusion that the influence of neutral salts is independent of the nature of the ester which

is hydrolysed, and that the correct explanation of such action will be such as does not involve the hydrolyte.

Experiments on the neutral salt action in solutions saturated with triacetin show that the effect is the same as in a homogeneous unsaturated system. H. M. D.

Action of Neutral Salts and the Concentration of the Catalyst. HUGH S. TAYLOR (*Medd. Vetenskapsakad. Nobelinst.*, 1913, 2, No. 35, 1—12).—The influence of potassium chloride on the catalytic activity of hydrochloric acid has been examined in a series of experiments on the rate of hydrolysis of ethyl acetate in aqueous solution. The concentration of the acid was varied from 0·01 to 0·5 mol. per litre, and in each case the effect of the addition of potassium chloride in 1 molar concentration was observed. The results indicate that the neutral salt effect Δ (see previous paper) increases regularly with increasing dilution of the acid from about 41% to 55%. The only exception occurs at the highest concentration of acid, but it is considered that this anomaly may be due to experimental error.

When a comparison is made between these numbers and the corresponding values obtained by earlier observers for the influence of neutral salts on the rate of the inversion of the sucrose at different acid concentrations, it is found that the variation of the salt effect with the acid concentration is much greater with sucrose as hydrolyte than with ethyl acetate. This result is apparently not in agreement with the view that the ratio of the catalytic activities of the hydrogen ion and of the undissociated acid is only dependent on the affinity constant of the acid, and independent of the solvent medium and the nature of the substrate. H. M. D.

The Catalytic Activity of the Undissociated Molecule. HUGH S. TAYLOR (*Medd. K. Vetenskapsakad. Nobelinst.*, 1913, 2, No. 37, 1—18).—Measurements have been made of the rate of hydrolysis of ethyl acetate in aqueous solution at 25° under the catalytic influence of trichloroacetic and dichloroacetic acids of varying concentration and in the presence and absence of the corresponding potassium salts. The data thus obtained, as well as those recorded in the two previous papers, are interpreted on the assumption that the catalytic action of the acid is due to the composite effect of the hydrogen ion and of the undissociated acid, as expressed by the formula $K = n_H\ K_H + n_M . K_M$, in which K is the observed velocity constant, n_H and n_M the concentrations of the hydrogen ion and the undissociated acid, and K_H and K_M the corresponding catalytic activities. By substitution of the experimental data in this equation, values have been obtained for the ratio K_M/K_H in the case of the three different acids.

The author states that the two sets of experiments with varying acid concentration and with and without neutral salt yield values for the ratio which are of the same order of magnitude. For hydrochloric acid the ratio is 2, for trichloroacetic acid, 0·35, and for dichloroacetic acid, 0·08. In the case of trichloroacetic acid

the separate values of the ratio are in much better agreement than those obtained for hydrochloric and dichloroacetic acids. In particular, it may be noted that the divergence in the case of dichloroacetic acid is very considerable, the tabulated values of the ratio being 0·16, 0·07, and 0·02.

The results are discussed in reference to the general theory of acid catalysis, and more particularly with regard to the presumed independence of the catalytic activity of the nature of the solvent and of the hydrolyte. H. M. D.

Catalysis by Cations. III. BROR HOLMBERG (*Zeitsch. physikal. Chem.*, 1913, **84**, 451—474. Compare A., 1912, ii, 443, 1048).—A continuation of the work described in Part II (*loc. cit.*). The hydrolysis of acetoxyacetic acid is studied in aqueous solution and in the presence of sodium hydroxide, barium hydroxide, and mixtures of these bases, also in the presence of hydrochloric and nitric acids. It is shown that the alkaline hydrolysis is a simple bimolecular reaction, the velocity constant of which is proportional to the seventh root of the concentration of the cation present. At 25° the catalysis constants are $C_{Na}=5·48$ and $C_{ba}=7·05$. When both sodium and barium ions are present together, the catalysis constant is given by the formula $C=(C_{Na}^{7}[Na^{\cdot}]+C_{ba}^{7}[ba^{\cdot}])^{1/7}$. In the acid hydrolysis the reaction is unimolecular, when so much of the catalyst is present that the concentration of the hydrogen ion is not reduced appreciably during the reaction. At 25° the relationship, between the velocity constant and the concentration of the hydrogen ion, is expressed by the formula $C=0·00044-0·108H^{\cdot}$. This formula is deduced on the assumption that the anion of acetoxyacetic acid is hydrolysed much more rapidly than the undissociated acid. The affinity constant of acetoxyacetic acid at 25° is calculated as $k=0·00122$. The paper concludes with a general theoretical discussion on cation catalysis, in which the author's views are stated. The views of Bredig, Acree, and Senter on this subject are stated and criticised. J. F. S.

The Effect of Ultra-violet Light on the Catalytic Activity of Colloidal Platinum. CHESTER J. FARMER and FREDERICK PARKER, jun. (*J. Amer. Chem. Soc.*, 1913, **35**, 1524—1527).—The authors find that ultra-violet light gradually destroys the catalytic activity of colloidal platinum. T. S. P.

The Structure of the Atom. Sir JOSEPH J. THOMSON (*Phil. Mag.*, 1913, [vi], **26**, 792—799).—The author describes an atom so constituted that the transformation of radiant energy into kinetic energy takes place according to Planck's law. It is shown that in such an atom the forces acting on a corpuscle in the atom are: (1) a radial repulsive force, varying inversely as the cube of the distance from the centre, diffused throughout the whole of the atom, and (2) a radial attractive force, varying inversely as the square of the distance from the centre, confined to a limited number

of radial tubes in the atom. It is shown that the photoelectric law follows as a consequence of these forces. The conversion of potential energy into radiant energy by the atom is considered mathematically. J. F. S.

Constitution of Atoms and Molecules. II. N. Bohr (*Phil. Mag.*, 1913, [vi], **26**, 476—502. Compare this vol., ii, 689).—This is an attempt to show that the application of Planck's theory of radiation to Rutherford's atom-model, through the hypothesis of the universal constancy of the angular momentum of the bound electrons, leads to agreement with experimental results. The evidence supports the view that the actual number of electrons in a neutral atom is equal to the number which indicates the position of the element in the series of elements arranged in order of increasing atomic weight—oxygen, the eighth element, for example, having eight electrons. The angular momentum of every electron round the centre of its orbit is assumed to be $h/2\pi$, where h is Planck's constant, and this, when the charge on the positive nucleus and the number of electrons in different rings is known, determines the configuration of the system, that is, the frequency of revolution and diameter of the rings. There will, however, be in general more than one stable configuration satisfying the conditions.

After a discussion on the configuration and stability of possible systems, the constitution of atoms containing very few electrons—hydrogen, one; helium, two; lithium, three; glucinum, four—is considered. The formula deduced for the frequencies of the hydrogen spectrum $\nu = K(1/\tau_2^2 - 1/\tau_1^2)$, where τ_1 and τ_2 are integers and $K = 2\pi^2e^4m/h^3$, gives for the constant K the value $3{\cdot}26 \times 10^{15}$, in agreement with the constant $3{\cdot}29 \times 10^{15}$ in the Balmer spectrum, and the calculated value for the diameter of the orbit a $0{\cdot}55 \times 10^{-8}$ is of the order of magnitude expected from the diameter of the hydrogen atom. The calculated potential required to ionise the atom is 13 volts, agreeing with the value found with positive rays, 11 volts.

For helium the frequency formula is the same, except that the integers τ_1 and τ_2 are replaced by $\tau_1/2$ and $\tau_2/2$. This gives the two spectrum series, hitherto associated with hydrogen, observed by Pickering for ζ Puppis, and by Fowler in vacuum tubes containing helium and hydrogen. Both electrons in the neutral helium atom are more firmly bound than the one in the hydrogen atom, and the calculated value for the ionisation potential is 27 volts. A helium nucleus with three electrons is unstable, indicating that the helium atom can never acquire a negative charge.

For lithium the spectrum corresponding with the removal of all three electrons should only be observed in extraordinary cases, owing to the great energy required, but in certain stars, showing the Pickering spectrum with special brightness, lines are observed corresponding with the formula. In this formula $\tau_1/3$ and $\tau_2/3$ replace τ_1 and τ_2 of the hydrogen spectrum, and the lines observed

correspond with $\tau_2=6$ and $\tau_1=10$, 13, and 14. With $\tau_2=1$, 2, or 3 only ultraviolet series are obtained, and for $\tau_2=4$, one line in the visible region (with $\tau_1=5$) of wave-length 4503, corresponding with a line 4504 of unknown origin, but there are no unidentified lines known with $\tau_2=5$. The most probable configuration for the lithium atom gives an outermost electron, bound even more lightly than for the hydrogen atom (ionising potential 1·4 volts), and two symmetrical inner electrons more strongly bound than in the helium atom. For glucinum two rings, each containing two electrons, the outer pair more lightly bound than for the helium atom, is deduced.

With various simplifying assumptions more complicated atomic structures are considered. For all numbers of electrons above 10 (neon) up to large numbers it is assumed that a ring of eight electrons occurs. A ring of sixteen electrons will not be stable until the number is large.

The characteristic X-radiation of an atom is assumed to be due to settling down of the system if electrons in the inner rings are removed, as by bombardment with cathode-rays, in contrast with the light-frequencies in which the outer rings are concerned. The theory leads to a formula for the velocity of the cathode-ray required to excite the characteristic X-radiation in an element, in agreement with Whiddington's experiments. Finally, radioactive phenomena are briefly discussed. F. S.

Some New Multiple Relations of the Atomic Weights of Elementary Substances; and the Classification and Transformations of Neon and Helium. HENRY WILDE (*Phil. Mag.*, 1913, [vi], **26**, 732—740 *).—The author divides the elements into seven groups, the atomic weights of which he states are multiples of one, two, three, four, five, six, and seven times that of hydrogen. Silicon he places in the group $n7$H, and he gives it the atomic weight 35, which he is of the opinion is supported by Dulong and Petit's law. The atomic weight of helium he places as 2; many other atomic weights are similarly changed. The recent experiments on the production of helium and neon from glass are explained by the author on the assumption that these elements are the primates of barium, lead and calcium, and silicon respectively. J. F. S.

Curious Atomic Weight Relations: Quaternian Series. FREDERICK H. LORING (*Chem. News*, 1913, **108**, 188—189).—In a previous paper (*ibid.*, 95) it has been pointed out that certain series of four elements exhibit secondary atomic-weight differences which form a geometrical progression. Such a series is represented by argon, iron, bromine, and silver. It is now suggested that helium, aluminium, manganese, and rubidium form a similar series, and that corresponding members of these two series are more or less closely related. Other series of the same type are formed by neon, nickel, tellurium, and an element of atomic weight 211·4, and

* and *Mem. Manchester Phil. Soc.*, 1913, **57**, No. XII., 1—11.

by an element of atomic weight 0·27, boron, magnesium, and potassium. H. M. D.

Valence and Tautomerism. WILLIAM C. BRAY and GERALD E. K. BRANCH (*J. Amer. Chem. Soc.*, 1913, **35**, 1440—1447).—Many chemists insist that the valence numbers of nitrogen in ammonia and ammonium chloride are 3 and 5 respectively, thus emphasising the total number of valence bonds, as illustrated by the usual structural formulæ. Others insist that the valence number of nitrogen is -3 in both cases, the valence number of hydrogen in its compounds being $+1$, and that of chlorine in chlorides -1. Two separate ideas are here involved, however, that of polarity and that of the total number of bonds. It seems advisable to retain the term valence for the two ideas, and the authors suggest the use of the distinguishing terms *polar* number and *total* valence number, whenever necessary. The valence of nitrogen in ammonium chloride can then be completely described as $(-3, 5)$, where, for convenience, the polar number is placed first.

Comparison of the properties of inorganic and organic substances leads to the conclusion that the nature of the union between two atoms may be either polar or non-polar in character, according as it is assumed that an electron passes completely or does not pass from one atom to the other. The non-polar character of certain organic compounds is well shown, for example, by comparison of the compounds methane and carbon tetrachloride. Their behaviour suggests that the valence of carbon is $(0, 4)$, that is, non-polar in both cases, since the assumption that they contain carbon with the valencies $(-4, 4)$ and $(+4, 4)$ respectively, would demand greater differences between the compounds than actually exist.

In the latter part of the paper tautomeric equilibria are discussed and classified on the basis of the valence changes involved. T. S. P.

Valence and Tautomerism. GILBERT N. LEWIS (*J. Amer. Chem. Soc.*, 1913, **35**, 1448—1455).—A discussion of the views put forward by Bray and Branch (compare the preceding abstract). T. S. P.

A Head to Prevent Spirting during Steam Distillations. JAMES J. POLAK (*Chem. Weekblad*, 1913, **10**, 870).—A description of a head for steam distillation. The steam from the boiler passes into the liquid in the flask through a tube sealed into a glass globe resembling an inverted flask with the usual neck. The steam escapes through this neck into the globe, and then passes to the condenser through a tube sealed into the top of the globe, the portion of this tube within the globe being bent out of the vertical to eliminate danger of spirting. A. J. W.

Inorganic Chemistry.

Recovery of Iodine from Residues. HAROLD W. GILL (*Analyst*, 1913, **38**, 409).—The following method, which depends on the solubility of sodium iodide in absolute alcohol, may be applied to the recovery of iodine from the waste solutions obtained in iodometric analysis, provided that the iodine has been dissolved originally in sodium iodide solution instead of potassium iodide solution. The residues are evaporated, heated in an air-oven until completely dry, and the coarse powder obtained is then extracted in a Soxhlet apparatus with absolute alcohol. The crystals of sodium iodide separated from the alcoholic solution may be recrystallised from alcohol, and in any case require to be dried first in an air-oven and afterwards under reduced pressure to expel traces of alcohol.

W. P. S.

The Glow of Sulphur. WALTER H. WATSON (*Chem. News*, 1913, **108**, 187—188).—Experiments are described relating to the phosphorescent glow which is exhibited by sulphur under certain circumstances. The glow is readily obtained when a current of air is passed over sulphur heated to a temperature below its ignition point, and then through a tube which is maintained at an appreciably lower temperature. Under these conditions the air becomes charged with sulphur vapour, which separates out in the form of a cloud of very small particles when the temperature falls. The oxidation of this finely-divided sulphur is the cause of the phosphorescence. There is no evidence of the formation of any other oxide than sulphur dioxide at any stage of the process. H. M. D.

Heterogeneous Equilibria in the System Sulphur Dioxide Halogen. TETTA POLAK-VAN DER GOOT (*Zeitsch. physikal. Chem.*, 1913, **84**, 419—450).—The fusion curves of the systems chlorine-sulphur dioxide, sulphur dioxide-sulphuryl chloride, chlorine-sulphuryl chloride, and the ternary system chlorine-sulphur dioxide-sulphuryl chloride have been determined. It is shown that the unexplained thermal effects observed by Smits and de Mooy (A., 1910, ii, 1049) were due to the presence of sulphuryl chloride which had been formed in the dark and in the absence of catalysts. In the chlorine-sulphur dioxide mixtures, which were rich in chlorine, mixed crystals were formed. The equilibrium

$$SO_2 + Cl_2 \rightleftharpoons SO_2Cl_2$$

was studied in the presence of various catalysts, of which camphor is shown to be the best, for in the liquid condition the two substances combine entirely to form sulphuryl chloride. The light catalysts could not be brought to an equilibrium. The solidification curve of sulphur dioxide and bromine was determined, and shown to be similar to that of sulphur dioxide-chlorine. Attempts were made to prepare sulphuryl bromide, but they were unsuccessful. J. F. S.

The Action of Sulphur Trioxide on Salts. WILHELM TRAUBE (*Ber.*, 1913, **46**, 2513—2524).—The author has devised a special apparatus by means of which anhydrous salts may be submitted to the action of sulphur trioxide, and then the products be completely freed from the excess of sulphur trioxide before being allowed to come into contact with the air. The amount of absorption occurring was determined by direct weighing in each case, and the products were analysed.

One molecule of sodium chloride absorbs two molecules of sulphur trioxide, with the formation of a hard, crystalline mass, which is considered to be *sodium chloropyrosulphonate*, $ONa\cdot SO_2\cdot O\cdot SO_2Cl$, sodium chlorosulphonate being probably an intermediate product in the reaction. It fumes in the air, and is decomposed by water, more slowly by alcohol. When added to a chloroform solution of diamylamine, diamylamine sulphamate is formed, which agrees with the formulation of the salt as a chloropyrosulphonate. No evidence of the existence of the product $NaCl(SO_3)_4$ (Schultz-Sellack, A., 1871, 193) could be obtained.

Ammonium chloride first liquefies under the action of sulphur trioxide, and then gives a crystalline product consisting of *ammonium chloropyrosulphonate*, $NH_4\cdot O\cdot SO_2\cdot O\cdot SO_2Cl$, which has properties similar to that of the sodium salt. It cannot be the hydrochloride of a sulphamic acid, since the latter is not found in solution when the salt is decomposed with alkalis.

Sodium nitrite swells up considerably when submitted to the action of sulphur trioxide, and then gives a colourless, crystalline mass, which is decomposed by water with vigorous evolution of oxides of nitrogen. Three molecules of sulphur trioxide are absorbed for each molecule of nitrite, the compound formed being probably *sodium nitrosotrisulphonate*, $NO_2(SO_3)_3Na$.

Persulphates absorb sulphur trioxide, at the same time losing some of their active oxygen, with the formation of what are probably *perpyrosulphates*, in accordance with the equation: $K_2S_2O_8 + 2SO_3 = KS_2O_6\cdot O_2\cdot S_2O_6K$. These compounds fume in the air, the fumes not consisting, however, of sulphur trioxide, and gradually deliquesce. No oxygen is evolved during the deliquescence, and the solution formed contains considerable quantities of hydrogen peroxide and persulphuric acid in varying proportions. When put into water the salts dissolve with violent hissing, and ozonised oxygen is evolved; the solution formed contains only traces of hydrogen peroxide and persulphuric acid. T. S. P.

Fluorosulphonic Acids and Its Salts. WILHELM TRAUBE (*Ber.*, 1913, **46**, 2525—2530).—In contradistinction to the salts described in the previous abstract, sodium fluoride reacts with sulphur trioxide, giving a product which does not immediately react with water with the formation of sulphuric acid. One molecule of sulphur trioxide is absorbed by one molecule of the salt, giving *sodium fluorosulphonate*, $F\cdot SO_3N_R$, which can be readily dissolved from unaltered sodium fluoride by extraction with alcohol. Ammonium fluoride reacts more readily than sodium

fluoride, and treatment of the reaction product with ammoniacal methyl alcohol gives a solution from which the well-crystallised *ammonium fluorosulphonate*, $F{\cdot}SO_3NH_4$, m. p. 245°, is readily obtained by evaporation. Other fluorides react similarly to the sodium and ammonium salts.

Simpler methods of preparing these salts were devised when it was found that not only they, but also fluorosulphonic acid (compare Thorpe and Kirman, T., 1892, **63**, 921), are fairly stable in aqueous solution. If ammonium fluoride is dissolved in fuming sulphuric acid and the solution heated, fluorosulphonic acid distils over; if the solution is treated with ammoniacal methyl alcohol and then separated from insoluble matter, which is chiefly ammonium sulphate, a solution of ammonium fluorosulphonate is formed, from which the solid salt is readily obtained.

Fluorosulphonates are formed not only when a dry mixture of fluorides and pyrosulphates is heated, but also when the two are mixed in the presence of a little water. The ammonium salt is readily obtained in this way. They can also be obtained by the direct action of alkali on an aqueous solution of fluorosulphonic acid, proving that the latter is not immediately decomposed by water.

Both sodium and ammonium fluorosulphonate react neutral to litmus. The aqueous solution of the latter is not completely decomposed even after keeping for days, and the salt can even be recrystallised from hot water. The salts are readily decomposed by warming with hydrochloric acid, or with alkalis. When distilled with 99% sulphuric acid, a good yield of fluorosulphonic acid is obtained.

When the sodium salt is heated in an atmosphere of carbon dioxide a gas is obtained which is not absorbed by potassium hydroxide in a short time, and which is probably sulphuryl fluoride (compare Moissan and Lebeau, A., 1901, ii, 233),

$$2F{\cdot}SO_3Na = Na_2SO_4 + SO_2F_2.$$

The compounds obtained by Weinland and Alfa (A., 1899, ii, 594) are not identical with the above salts. T. S. P.

The Atomic Weight of Selenium. JOSEF JANNEK and JULIUS MEYER (*Zeitsch. anorg. Chem.*, 1913, **83**, 51—96; *Ber.*, 1913, 46, 2876—2882).—The decomposition of selenious acid into selenium dioxide and water begins below 50°, but even at this temperature selenium dioxide has an appreciable vapour-pressure. The molecular heat of hydration of selenium dioxide is 3192 cal. The vapour-pressure of selenium, determined by Ruff and Graf's dynamic method (A., 1907, ii, 947), is found to be extremely small, so that at 170—220° volatilisation is inappreciable. Crystalline selenium is quite insoluble in water.

As it is impossible to prepare anhydrous selenium dioxide by sublimation of the acid, the oxidation of selenium (purified by reduction from selenious acid by sulphurous acid, hydrazine sulphate, or hydroxylamine hydrochloride) with nitrogen peroxide has been employed. Nitric and hydrochloric acids and water are

purified by distillation from silica vessels. Hydrazine hydrate is distilled from a platinum flask, and kept in a silver vessel in a desiccator.

Oxidation of selenium with nitric acid gives selenic acid. To obtain selenium dioxide from this, it is necessary to add some hydrochloric acid during oxidation or before sublimation; otherwise the product is coloured. In any case it retains water.

Commercial nitrogen peroxide is purified by passing over hot copper oxide, condensing, passing air through the liquid, and distilling from silver nitrate to remove chlorine. A current of dry oxygen, charged with nitrogen peroxide, is then passed into a weighed silica vessel containing selenium, the temperature of which is at first 215°, and is gradually raised above the melting point of selenium. After oxidation is complete, the nitrogen peroxide is removed by dry air, and the dioxide sublimed a second time and weighed. Attempts to reduce the product to selenium by means of dry gases are unsuccessful, but hydrazine hydrate reduces it quantitatively, the original selenium being very exactly recovered.

The value, corrected to vacuum, found for the atomic weight of selenium is 79·141.

For the colorimetric estimation of selenium, sodium hyposulphite gives a sensitiveness of 0·005% SeO_2 in water, or 0·002% in concentrated sulphuric acid, whilst with potassium iodide and starch even 0·0000005 gram SeO_2 in 1 c.c. of solution may be detected, or five times that quantity in concentrated sulphuric acid.

Concentrated hydrazine hydrate and selenious acid yield a red solution containing hydrazonium selenite and polyselenides, which on dilution forms very stable colloidal selenium. C. H. D.

Preparation of Tellurous Acid and Copper Ammonium Tellurite. G. O. OBERHELMAN and PHILIP E. BROWNING (*Amer. J. Sci.*, 1913, [iv], **36**, 399—400).—Tellurous acid may be obtained from the residues from the electrolytic refining of copper as follows: The residues are treated with a solution of ammonium hydroxide, and the tellurous acid precipitated from the solution so obtained by means of acetic acid (compare Browning and Flint, A., 1909, ii, 934). By dissolving the tellurous acid thus obtained in sodium hydroxide and precipitating again by acetic acid, copper and many other metals, the hydroxides of which are insoluble in sodium hydroxide, are removed.

If the precipitation of the tellurous acid by acetic acid is brought about without warming the solution, and the product is dried without heating, the tellurous acid obtained is readily soluble in the alkali hydroxides. If, however, the precipitation takes place in hot solution and the precipitate is dried by the application of heat, the product tends to be quite insoluble in the alkali hydroxides.

After the first treatment of the residues with ammonia in this extraction process it was observed that a purple, crystalline salt separated from the alkaline solution on keeping. A similar salt could be obtained by allowing an ammoniacal solution of tellurous

acid containing some copper salt to evaporate over sulphuric acid and in the presence of soda lime; also, by adding slowly, with constant stirring, acetic acid to an ammoniacal solution of tellurous oxide and copper chloride. This salt, on analysis, gave TeO_2,83·84, CuO,4·63, NH_3,5·22, H_2O,6·10, and is a *copper ammonium tellurite*.

Similar salts could not be obtained with nickel, cobalt, zinc, cadmium, or silver in the place of copper. T. S. P.

Influence of Various Conditions on the Oxidation of Nitrogen in the Voltaic Arc. ALEXEI V. SAPOSHNIKOV, A. GUDIMA, and V. KUTOVSKI (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1076—1091).—Experiments made with an arc passing between carbon electrodes show that, as the air-supply, V (cub. metres per hour), is increased, the ratio of V to the power consumed, KW, also increases. The yield of nitric acid per kilowatt-hour at first increases to a maximum of 65·3 grams for $V : KW$ = about 1, then diminishes somewhat, and finally increases again to 78 grams per kilowatt-hour for a value 1·90 of the ratio $V : KW$. With both dry air and air saturated with moisture, the percentage of nitric oxide in the issuing gases increases to a maximum, and then decreases as the air-supply is continuously increased, but the wet air gives the higher yields in all cases, the difference in yield diminishing as the air-supply increases. The action of the moisture is probably expressed by the equations: $N_2 + 2H_2O = 2NO + 2H_2$ and $2H_2 + O_2 = 2H_2O$.

As material for the electrodes, carbon is greatly to be preferred from an industrial point of view. It gives a very constant arc, requires no cooling arrangement, and allows of the ready introduction into the arc of extraneous substances; it burns away rapidly, but this may be avoided by coating the lateral surfaces electrolytically with nickel. Of metallic electrodes, those of copper give the best results, whilst the use of platinum is not to be recommended. T. H. P.

Combustion of Air in the Voltaic Arc. ALEX. I. GORBOV and V. F. MITKEVITSCH (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1109—1136).—The principal conclusions arrived at by the authors as a result of theoretical considerations and of experimental data obtained with a small Birkeland-Eide furnace and with one of their own design, are as follows:

The relation between c, the percentage of nitric oxide formed on combustion of air under the influence of the voltaic arc, δ, the volume of air introduced into the furnace per hour per kilowatt, and G, the number of grams of nitric acid into which the nitric oxide may be transformed, is expressed by the equation

$$8G/225 = c\delta \quad \text{(I)},$$

which is similar in form and in the significance of its terms, to the Clapeyron gas equation, $RT = pv$. From this it follows that (1) if with a given air-supply the conditions of combustion are changed so as to maintain a certain definite percentage of nitric oxide, the number of grams of nitric acid per kilowatt-hour will be the greater

the less the number of kilowatts supplied to the arc, and (2) one and the same quantity of nitric acid per kilowatt-hour may be obtained with various concentrations of nitric oxide, if with constant arc-power and variable conditions of burning the percentage of nitric oxide changes in inverse proportion to the air-supply.

The general relationship between the air-supply and the percentage of nitric oxide in the issuing gas may be derived a priori on the assumption that the divergence of technical apparatus from the ideal is expressible as a certain air-supply to be applied as a correction to that actually used. The conclusion thence drawn is that, with the limits in concentration of nitric oxide as yet attainable in practice, this relationship is expressed by the hyperbolic formula $c=b/(\delta+a)$ (II). Writing b' for b/a, this gives $G=225a(b'-c)/8$ (III) and $G=225b\delta/8(\delta+a)$ (IV). These equations are regarded as general, and are probably applicable to the data obtained with any electric furnace.

Comparison of equation (III) with the fact that a furnace may work with a constant yield of nitric acid, but with a variable percentage of nitric oxide, leads to the conclusion that, for each furnace, there is possible not a single equation of type (III), but a series of them corresponding with varying utilisation of the energy. In agreement with the observations of other investigators, it is found that the values of a'' and b'', a''' and b''', etc., for this series of equations exhibit a constant ratio, that is,

$$b''/a''=b'''/a'''= \ . \ . \ . \ =\text{const.}=b'.$$

In the diagram representing the values of G as ordinates and the corresponding ones of c as abscissæ, each furnace is represented by a group of straight lines beginning in the point b' and spreading upwards from right to left in the shape of a fan. The constancy of b' does not follow immediately from the above equations, but is found to be in agreement with the fundamental hypothesis expressed by $c=b/(\delta+a)$.

A further conclusion drawn from the experimental data is that the concentration of nitric oxide on breaking of the arc is independent of the power of the arc, and almost independent of the detailed construction of the furnace, although characterised by its type; such a conclusion is, however, based on a comparatively small number of results.

The magnitudes of b and b' are regarded as characterised principally by the density of the energy in the region where the nitric oxide is formed, and the technical plant now in use leaves considerable room for increasing them; the magnitude of a should be as small as possible. T. H. P.

The Action of Finely Divided Nickel on Nitric Oxide. R. S. Felgate (*Chem. News*, 1913, **108**, 178).—Nitric oxide can be catalytically decomposed by finely divided nickel suspended in hot water, the products of decomposition being nitrogen and nickel oxide. The nickel should be prepared by the reduction of the dry precipitated hydroxide in an atmosphere of hydrogen.

Colloidal nickel prepared by Bredig's method does not act in a

similar manner. The action appears to depend on the state of aggregation and method of preparation of the nickel catalyst, but further investigation of this point is necessary. T. S. P.

Hydrazine and Its Inorganic Derivatives. I. Hydrazine Nitrites and Their Decomposition Products. FRITZ SOMMER (*Zeitsch. anorg. Chem.*, 1913, **83**, 119—137).—*Hydrazine nitrite*, $N_2H_5NO_2$, may be prepared by mixing solutions of barium nitrite and neutral hydrazine sulphate, stirring to convert the thick, gelatinous barium sulphate into the crystalline form, and filtering by means of a vacuum. The stable solution is then evaporated in a vacuum over phosphoric oxide. The oil thus obtained does not crystallise spontaneously, but does so on inoculating with a small quantity of solid obtained by extracting a portion with methyl alcohol, partly precipitating with ether, and cooling in ether and solid carbon dioxide. The solid salt is almost white, but becomes yellow on fusion. It is hygroscopic, and dissolves readily in alcohol, but not in ether, and may be obtained from a mixture of these in large, probably monoclinic prisms. It explodes violently with a blow, less vigorously if rapidly heated.

For analysis, hydrazine is estimated with iodine by Stollé's method (A., 1903, ii, 100). The same solution, after the addition of solid potassium iodide, is mixed with a known quantity of dilute sulphuric acid in an atmosphere of carbon dioxide. The iodine liberated according to the equation

$$2HNO_2 + 2HI = 2NO + 2H_2O + I_2$$

is then titrated with thiosulphate.

The salt decomposes according to the equation

$$N_2H_5NO_2 = NH_3 + N_2O + H_2O,$$

and this decomposition is very greatly accelerated by nitrous acid. The preparation of hydrazine dinitrite in aqueous solution is thus impossible, as the weakly basic character of hydrazine would cause the salt to be so far hydrolysed that much nitrous acid would be present in the solution. If hydrazine disulphate and barium nitrite react together, the products are ammonium nitrite and nitrous oxide. The decomposition of hydrazine nitrite is thus due to the action of nitrous acid on the undissociated compound, and is autocatalytic. The secondary reaction, the formation of hydrazoic acid from hydrazine and nitrous acid, is due to the action of nitrous acid on the N_2H_5 ion.

Under similar conditions hydrazine nitrite is less stable than ammonium nitrite, but aqueous solutions of the former are the more stable, as the traces of ammonia first formed check the hydrolysis.

The failure to obtain the compound from barium nitrite and ordinary hydrazine sulphate (Dey and Sen, A., 1911, ii, 822) is due to the fact that the latter substance is mainly the disulphate, which behaves as an acid salt. The normal sulphate, prepared by digesting the ordinary salt with barium carbonate, forms perfectly stable, hexagonal crystals, $(N_2H_5)_2SO_4,H_2O$, which dissociate into the anhydrous salt and water at 47·3°. The anhydride has m. p. 117°.

The method of Dey and Sen for the detection of nitric in presence of nitrous acid (A., 1912, ii, 296) is not exact. The diphenylamine test should not be applied until the excess of hydrazine has been destroyed, as otherwise the blue colouring matter may be reduced by the hydrazine. C. H. D.

Preparation of Phosphonium and Ammonium Iodides and the Action of Heat on those Substances. ALFRED HOLT and JAMES E. MYERS (*Zeitsch. anorg. Chem.*, 1913, **82**, 278—282. Compare P., 1913, **29**, 61).—Phosphonium iodide may be prepared by distilling purified iodine with fused calcium nitrate, and allowing it to react with a solution of phosphorus in carbon disulphide, thoroughly dried by anhydrous sodium sulphate, the reaction taking place in an atmosphere of nitrogen. The best results are obtained by using a minimum quantity of solvent and adding the iodine in the solid form. The iodide thus obtained may be sublimed without decomposition. It retains some of the water used in its preparation, and may be dried by subliming through a column of phosphoric oxide in an apparatus which is described.

Hydrogen phosphide, purified by conversion into and decomposition of its compound with cuprous chloride, is freed from hydrogen chloride, dried by phosphoric oxide, and allowed to react with hydrogen iodide, prepared from potassium iodide and metaphosphoric acid, and purified by means of red phosphorus and phosphoric oxide, followed by liquefaction and fractionation.

A third method consists in combining iodine vapour with yellow phosphorus and adding the required quantity of water.

The yellow tint of phosphonium iodide which has been distilled is not due to iodine, but to a phosphorus iodide, which yields phosphoric acid with water. Phosphonium iodide may be distilled without discoloration in a moist inert gas or in steam.

Ammonium iodide does not form nitrogen iodide under similar conditions. C. H. D.

Modifications of Arsenic. I. Grey and Brown Arsenic. VOLKMAR KOHLSCHÜTTER, E. FRANK, and CURT EHLERS (*Annalen*, 1913, **400**, 268—301).—The differences in the natural forms of solid substances of the same composition may be due to differences in crystalline structure, to chemical isomerism, or to various physical and chemical factors which impress on the substance a definite form during the process of its formation; for example, of the modifications of carbon, the diamond and graphite are each sharply defined, but the appearance of amorphous carbon is influenced by the various factors operating during its process of formation. The present research has brought to light the importance of certain factors in determining the form of a substance during its process of formation; one factor of especial importance is the original state of distribution of the molecules of the material which is undergoing change. Many substances, which are generally regarded as monotropic modifications, are certainly only one and the same substance in different states of distribution.

Well-known forms of arsenic are (i) "metallic," hexagonal arsenic, D 5·73; (ii) yellow arsenic, D^{18} 2·03, crystallising in the regular system; (iii) grey or black arsenic, D 4·60—4·72, obtained in arsenic mirrors; (iv) brown arsenic, D 3·7—4·7, obtained by the reduction of arsenic compounds in aqueous solution or by the action of oxygen or arsenious bromide on yellow arsenic dissolved in carbon disulphide. Erdmann (A., 1908, ii, 584) regards the differences in these four modifications as being due to differences in molecular complexity, and represents metallic arsenic, the densest modification, as consisting of monatomic molecules.

The authors are of opinion that yellow arsenic (specific volume 0·5), in comparison with metallic arsenic (sp. vol. 0·175), is the same quantity of matter distributed throughout a very much larger space, and the conversion of yellow into metallic arsenic is a process of condensation, analogous to that which obtains in the formation of silver from silver oxide (Kohlschütter and Eydmann, this vol., ii, 589). Such a process offers the best of opportunities for a substance to be obtained in different modifications. The conversion of yellow into metallic arsenic has been studied from this point of view, attention being particularly directed to the production of the intermediate forms, grey and brown arsenic.

Grey arsenic is obtained by the action of light on yellow arsenic prepared either from carbon disulphide solution or by the sublimation of metallic arsenic. The formation of the grey arsenic is the more rapid the finer is the state of division of the yellow arsenic; it collects on the walls of the vessel as a grey or black mirror, only a little being obtained in the form of a dust. It has D^{18} 4·69—4·707, and is amorphous. Reasons are given for the authors' belief that grey arsenic is only metallic arsenic in a finer state of distribution, that is, the same matter occupying a larger space.

Brown arsenic is obtained in various ways by the reduction of arsenic compounds. It changes directly to metallic arsenic by heating. The purest brown arsenic obtained by the authors has D 4·52, and there is no doubt that the densities of grey and of brown arsenic, free from all impurities, are nearly the same, so that the density is not a sufficient criterion to distinguish these substances as different modifications. The authors' experiments indicate that grey and brown arsenic are simply the same modification of metallic arsenic in different states of distribution, that of brown arsenic being the more diffuse. Brown arsenic is only obtained under the influence of a foreign substance which acts in a certain sense as a dispersing medium, the nature and concentration of which determines the state of distribution. C. S.

The Oxidisability of Charcoal at Moderate Temperatures. KARL A. HOFMANN, K. SCHUMPELT, and K. RITTER (*Ber.*, 1913, 46, 2854—2864).—It has previously been shown (this vol., ii, 609) that amorphous carbon is oxidised by chlorate solutions at water-bath temperature in the presence of osmium tetroxide, to carbon dioxide, mellogen, and mellitic acid. Further experiments have shown that the oxidisability of carbon at medium temperatures is much greater

than hitherto supposed, and details are given of the action of chlorate solutions on various charcoals.

In dilute aqueous solution calcium hypochlorite acts so vigorously on various charcoals, with foaming evolution of carbon dioxide, that the energy of oxidation of the system is available in a few seconds, and the heat produced can be used, under proper conditions, for steam raising, etc. The results of calorimetric measurements with different charcoals are given.

The carbon dioxide evolved is always accompanied by carbon monoxide (compare Rhead and Wheeler, T., 1912, **101**, 846) in amounts up to 9%. The occurrence of this gas is explained by the formation of high-molecular carbonyl compounds as intermediate products, the presence of such compounds being indicated by the deep brownish-black to red, fluorescent solutions obtained during the reactions; further oxidation gives carbon monoxide and dioxide. In contradistinction to the black, amorphous varieties of carbon, powdered diamond, on treatment with hypochlorite solution, gives a *white* suspensoid, which is to be further investigated; the diamond is attacked only to a slight extent.

When black, amorphous carbon of various kinds is exposed to the air at 120—150° in the presence of alkalis, it gives, at first, dark brown to red colloids, which are then oxidised to formate and oxalate, and finally to carbonate.

Neglecting the different initial velocities of reaction, the different kinds of amorphous carbon react so similarly towards oxidising agents that no essential difference in chemical structure can be assigned to them. T. S. P.

The Action of Hydroxyl Ions on Silicates. PAUL ROHLAND (*Zeitsch. anorg. Chem.*, 1913, **83**, 138—142).—The coagulation of emulsions of kaolin or clay by salts depends on the concentration of hydroxyl ions. The coagulating effect increases with the hydroxyl concentration to a maximum. Cement and other silicates are similarly affected. Other physical factors are involved.

C. H. D.

The Action of Sulphur Monochloride on Certain Minerals. HIRAM STANHOPE LUKENS (*J. Amer. Chem. Soc.*, 1913, **35**, 1464—1469). —The author has investigated the action of sulphur monochloride, at different temperatures up to about 800°, on the following minerals: felspar, garnet, zircon, sphene, tourmaline, hornblende, pyroxene, spinel, rhodonite, and pyromorphite. Only those which contained a considerable quantity of elements the chlorides of which are volatile in sulphur monochloride were acted on to any marked extent. Garnet and sphene may be almost completely decomposed in this way, and iron completely removed from zircon. Pyromorphite is completely decomposed at 450—550°, the residue then being soluble in dilute hydrochloric acid, with the exception of any silica which may be present. T. S. P.

Potassium Ammonomagnesate, $Mg(NHK)_2,2NH_3$. EDWARD C. FRANKLIN (*J. Amer. Chem. Soc.*, 1913, **35**, 1455—1464).—*Potassium ammonomagnesate*, $Mg(NHK)_2,2NH_3$, a new salt belonging to the author's ammonia system of acids, bases, and salts (compare A., 1912, ii, 451), has been prepared by the action of potassium amide in liquid ammonia solution on magnesium iodide, magnesium nitrate, magnesium acetamide, and magnesium respectively, the reactions taking place according to the equations:

$$MgI_2,(NO_3)_2,(MeCONH)_2+4KNH_2= Mg(NHK)_2,2NH_3+2KI,(NO_3),(MeCONH)$$

and $Mg+2KNH_2+2NH_3=Mg(NHK)_2,2NH_3+H_2$. The preparation was carried out by the methods previously described for similar compounds.

Potassium ammonomagnesate is a fine, crystalline powder, which is only slightly soluble in liquid ammonia, and is rapidly hydrolysed by liquid water or water vapour. It is not explosive, and may be heated to 100° without loss of ammonia.

For the purpose of the preparation it was necessary to obtain anhydrous magnesium iodide, nitrate, and acetamide. The first two were obtained by the action of magnesium on liquid ammonia solutions of ammonium iodide and nitrate respectively, hydrogen being evolved with the formation of the compounds *magnesium hexammine iodide*, $MgI_2,6NH_3$, and *magnesium hexammine nitrate*, $Mg(NO_3)_2,6NH_3$. Magnesium acetamide has been described by Franklin and Stafford (A., 1902, i, 748). T. S. P.

Potassium Hydroxopentafluorostannate [Stannihydroxopentafluoride]. SAMUEL H. C. BRIGGS (*Zeitsch. anorg. Chem.*, 1913, **82**, 441—444).—The salt K_2SnF_6,H_2O, prepared from stannic chloride and potassium fluoride, and crystallising in octahedra, has been described by Marignac, who also assigned the same formula to a salt crystallising in lamellæ, and obtained from the former by the addition of potassium hydroxide. This salt is now shown to be

$$K_2(SnF_5OH),H_2O.$$

Potassium carbonate is preferable to the hydroxide. The salt forms highly glistening leaflets, and is more soluble than the hexafluoro-compound. An anhydride, probably $K_4(SnF_5\cdot O\cdot SnF_5)$, is formed at 160—170°. C. H. D.

Crystallisation of Sodium Chloride, Bromide, and Iodide from Fusion and Aqueous Solution. E. SCHOBERT (*Jahrb. Min.*, 1913, ii, *Ref.* 186—187; from *Diss.*, Leipzig, 1912).—The three binary systems of sodium haloids were investigated. The melting points of the simple salts are: the chloride, 800° (Walther and White), bromide, 748°; iodide, 670°.

NaCl–NaBr.—When fused together, these form a continuous series of mixed crystals, with a minimum at 731° and NaBr 72 mol. %. From solution the chloride crystallises below 0·15° as the dihydrate $NaCl,2H_2O$ in six-sided plates; and the bromide forms the monoclinic dihydrate $NaBr,2H_2O$ below 50·7°. The hydrated and the anhydrous salts each form mixed crystals; at

and the series Na(Cl,Br) is continuous, but at -10° there is a break in the mixed crystals of the dihydrates. At 15° anhydrous or hydrated crystals appear according to the ratio of chloride to bromide in the solution.

NaBr-NaI.—Fusions give a continuous series of mixed crystals, with a minimum at 636° and NaI 67 mol. %. These mixed crystals are unstable, becoming cloudy at the ordinary temperature. The hydrates, $NaBr,2H_2O$ and $NaI,2H_2O$, are both monoclinic, although of different habit, and they do not form mixed crystals.

NaCl-NaI.—These give a eutectic at 570° with NaI 62·5 mol. %. The chloride separates with a maximum isomorphous intermixing of NaI 2—3 mol. %; and the iodide with NaCl 24 mol. %. From solution at 60° pure sodium chloride cubes separate even in the presence of much iodide; and at lower temperatures there is no appreciable isomorphous mixing. L. J. S.

Colloidal Metal Chlorides and Sulphates. László Karczag (*Biochem. Zeitsch.*, 1913, **56**, 117—121).—When sodium salicylate is treated with thionyl chloride, the sodium chloride resulting from the reaction, $OH\cdot C_6H_4\cdot CO_2Na + SOCl_2 = OH\cdot C_6H_4\cdot COCl + NaCl + SO_2$, separates in a colloidal form. The sodium salt of benzoic and other acids on similar treatment also yield sodium chloride in a colloidal form, and chlorides of other metals can also be obtained by using salts of metals other than sodium. The appearance and properties of these colloids can be varied by varying the conditions, such as using indifferent solvents like benzene or light petroleum. These colloids can also be dissolved in certain indifferent solvents, from solutions in which they can be precipitated by other liquids. By using sulphuryl chloride instead of thionyl chloride, metallic sulphates can be obtained in colloidal form. S. B. S.

Theory of the Causticising of Alkali Carbonate Solutions. P. P. Fedotéev (*Zeitsch. anorg. Chem.*, 1913, **82**, 341—352).—The reaction $Na_2CO_3 + Ca(OH)_2 \rightleftharpoons 2NaOH + CaCO_3$, has been studied, using the experimental data of Wegscheider and Walter (A., 1907, ii, 259, 686), with some data from other authors. An equilibrium diagram is constructed for 80°, the solid phases being $Ca(OH)_2$, $CaCO_3$ and $CaCO_3,Na_2CO_3,2H_2O$ (pirssonite). The end of the mass-action curve lies at 80° on the line of total sodium concentration corresponding with 5·3 equivalents Na. The concentration of the solution at this point is $\Sigma OH = 4{\cdot}3$ and $\Sigma CO_3 = 0{\cdot}5$ mols. per litre. A shaded area in the diagram, within which causticising is technically performed, is so situated that a double salt is not deposited, even when the temperature falls greatly during settling and cooling. C. H. D.

Bromides. V. Icilio Guareschi (*Atti. R. Accad. Sci. Torino*, 1913, **48**, 929—947. Compare this vol., ii, 692).—The present paper deals with the four bromides: $CaBr_2,6H_2O$, $SrBr_2,6H_2O$, $BaBr_2,2H_2O$, and $CoBr_2,6H_2O$. By keeping them under various conditions (at various temperatures, in the presence or absence of

dehydrating agents, and with or without the use of a current of dry air) until of constant weight, a number of hydrates can be obtained.

In the case of calcium bromide, hydrates exist containing $6H_2O$, $5H_2O$, $4H_2O$, $3H_2O$, $1\frac{1}{2}H_2O$, $1H_2O$, and $\frac{1}{2}H_2O$. Strontium bromide forms two hydrates: $SrBr_2,6H_2O$ and $SrBr_2,H_2O$. Barium bromide exists in the two hydrated forms: $BaBr_2,2H_2O$ and $BaBr_2,H_2O$.

Cobaltous bromide exists in the following forms (compare Hartley, this Journal, 1874, **27**, 501): $CoBr_2,6H_2O$ (red prisms, m. p. 47—48°); $CoBr_2,5\frac{1}{2}H_2O$ (?) (rose-coloured); $CoBr_2,5H_2O$ (pink); $CoBr_2,4H_2O$ (reddish-violet, m. p. 70—71°); $CoBr_2,2H_2O$ (reddish-violet); $CoBr_2,H_2O$ (blue); $CoBr_2,\frac{1}{2}H_2O$ (?); $CoBr_2$ (anhydrous, green). R. V. S.

Supposed Occurrence of a Peroxide in Calcium Hydroxide Exposed to the Action of Air. HUGO DITZ (*J. pr. Chem.*, 1913, [ii], **88**, 443—456. Compare this vol., ii, 320).—The author adversely criticises Vaubel's work (A., 1912, ii, 1180; this vol., ii, 706) on the occurrence of a peroxide in calcium hydroxide after exposure to air, and maintains that the benzidine, *m*-phenylenediamine and starch-iodide reactions, used by Vaubel for the detection of the peroxide, are not suitable for this purpose. The starch-iodide reaction cannot be used in the presence of iron, the small amount of iron present in calcium hydroxide being sufficient to cause the rapid development of the blue colour.

The reaction with benzidine is probably due to the presence of manganese in the calcium hydroxide, whilst the *m*-phenylenediamine reaction cannot be used for the detection of peroxides in the presence of iron and manganese.

On the other hand, the titanic acid reaction is not influenced by the presence of calcium hydroxide as stated by Vaubel; a specimen of calcium hydroxide, which gave no reaction with this reagent, at once developed an intense yellow coloration on the addition of a trace of hydrogen peroxide. Even after 100 days' exposure to air, no trace of peroxide could be detected in the calcium hydroxide.

The author accordingly reaffirms his view that the starch-iodide and other reactions shown by calcium hydroxide are due to traces of manganese and iron, or to the formation of nitrite by the action of nitrous acid in the air (compare following abstract). F. B.

Occurrence and Manner of Formation of Nitrite and Nitrate in Calcium Hydroxide and Other Compounds Exposed to the Action of Air. HUGO DITZ and FRANZ KANHÄUSER (*J. pr. Chem.*, 1913, [ii], **88**, 456—479).—The author has previously expressed the view (this vol., ii, 320) that the increase in the intensity of the starch-iodide reaction, shown by calcium hydroxide on exposure to air, is probably due to the gradual formation of nitrite by the absorption of the nitrous acid from the air, since, after exposure, nitrites can be detected by means of α-naphthylamine and sulphanilic acid. It is now found that

both nitrite and nitrate are produced, and their amounts have been determined after varying times of exposure. A specimen of calcium hydroxide, after twelve days' exposure to the laboratory atmosphere, contained nitrite corresponding with 0·020% of nitrous acid, and this amount did not appreciably increase even after exposure for forty days.

The formation of nitrites and nitrates by exposing calcium carbonate and other basic substances to air has already been investigated by Baumann (A., 1889, 183), who has shown that the nitrous and nitric acids concerned in the formation of the nitrites and nitrates are not produced by the oxidation of atmospheric nitrogen or ammonia in the presence of the basic substances, but are already pre-existent in the atmosphere, and probably owe their origin to the direct union of nitrogen and oxygen during the combustion of coal gas and other combustibles used in the laboratory for heating and lighting purposes. The author describes a series of experiments carried out with calcium hydroxide in support of this view.

F. B.

Artificial Formation of Dolomite. K. Spangenberg (*Zeitsch. Kryst. Min.*, 1913, **52**, 529—567).—Working on the lines suggested by Linck (A., 1911, ii, 294), solutions of calcium and magnesium chlorides and ammonium sesquicarbonate were experimented on in an atmosphere of carbon dioxide at various temperatures and pressures. Under the various conditions, dolomite, calcite, magnesite, or vaterite were obtained. Dolomite, D 2·825, was best prepared by the action of magnesium chloride and sodium carbonate solutions on vaterite at 180—200° in 50 atmospheres of carbon dioxide. Dolomite and calcite may be separated by means of a solution of copper nitrate.

L. J. S.

Solubility of Calcium Sulphite. Jules Robart (*Bull. Assoc. chim. Sucr. Dist.*, 1913, **31**, 108—111).—In experiments carried out with the object of ascertaining the solubility of calcium sulphite in various solutions, 1 litre of the solution containing the reagents, etc., was in each case boiled for three minutes, filtered at a temperature of 100°, and, after cooling, the amount of lime in the filtrate was estimated. One litre of water dissolved a quantity of calcium sulphite equivalent to 78 mg. of calcium oxide; this quantity was diminished to 37 mg. in the case of a 12% sugar solution. The presence of calcium carbonate causes a slight increase in the solubility of the sulphite, but when alkali hydroxides, carbonates, and sulphites are present, practically no calcium salts dissolve. With respect to sulphited sugar liquors, it is recommended that these should be filtered while hot, as the solubility of calcium sulphite increases when the temperature is lowered.

W. P. S.

The Binary System $CaSiO_3$–CaF_2. Franz Tursky (*Zeitsch. anorg. Chem.*, 1913, **82**, 315—322. Compare Karandéeff, A., 1910, ii, 954).—When the quantity of calcium fluoride is small, the

fluorine is completely volatilised on melting, larger quantities are partly retained as fluoride, but solid solutions are not formed in any case. Pseudowollastonite is obtained at high temperatures, but when the proportion of calcium fluoride is sufficient, wollastonite is obtained. In nature, the latter mineral can only have been formed in presence of mineralisers, such as fluorides. C. H. D.

Filtration of Barium Sulphate. J. L. OSBORNE (*J. Physical Chem.*, 1913, **17**, 629—631).—Experiments are described which confirm the observation that barium sulphate can be filtered quite readily under suction if a concentrated solution of ammonium acetate is added to the precipitate and the mixture well stirred before filtration. The experiments show further that the coagulating effect of the ammonium acetate is dependent on the solubility of barium sulphate in concentrated ammonium acetate solution. In presence of ammonium chloride or hydrochloric acid, the effect of the ammonium acetate is less evident, and this is attributed to the lowering of the solubility of barium sulphate in presence of these substances. H. M. D.

Experiments at High Temperatures. I. Fusion and Volatilisation of Refractory Oxides in the Electric Vacuum Furnace. OTTO RUFF, HERMANN SEIFERHELD, and JOSEPH SUDA (*Zeitsch. anorg. Chem.*, 1913, **82**, 373—400. Compare A., 1910, ii, 575).—The melting point of most refractory oxides in a carbon furnace depends in a high degree on the character of the surrounding atmosphere. The only oxide which has a sufficiently well-defined melting point under the conditions employed to serve for calibration purposes is alumina ($2010 \pm 10°$).

Glucinum oxide, GlO, has m. p. 2525° under reduced pressure, but volatilises below that temperature. Magnesia melts above 2500°, but reacts vigorously with carbon, so that the true temperature has not been determined. Lime also reacts with carbon and nitrogen. Under reduced pressure it is not melted at 2150°, but volatilises rapidly from 2000° onwards. Zirconia is readily reduced, but the lower oxide formed has m. p. 2585°, almost independent of the pressure or of the rate of heating. Its vapour pressure is very low, even at the melting point. Stannic oxide melts in a zirconia crucible at 1625°, and is at once violently reduced.

The oxides of yttrium, cerium, thorium, and lanthanum are rapidly converted into carbides. Titanium dioxide is completely converted in a short time into the oxide Ti_7O_{12}. Columbium, tantalum, and chromium oxides are reduced to lower oxides. C. H. D.

Glucinum Compounds. WILHELM BILTZ (*Zeitsch. anorg. Chem.*, 1913, **82**, 438—440. Compare Mieleitner and Steinmetz, this vol., ii, 707).—Crude glucinum sulphide, prepared from the metal and sulphur vapour, is strongly phosphorescent.

Glucinum and scandium acetylacetonates have the simple

molecular weight in carbon disulphide solution, and are unchanged in the presence of ammonia, thus resembling aluminium rather than the rare earths.

Potassium glucinum fluoride, K_2GlF_4, crystallises from solutions having the composition $KGlF_3$. C. H. D.

The Corrosion of Lead in Lime Mortar, and the Supposed Peroxide Occurring in Calcium Hydroxide which has been Exposed to the Air. HUGO DITZ (*Zeitsch. angew. Chem.*, 1913, 26, 596—598).—Polemical against Vaubel (A., 1912, ii, 1172; this vol., ii, 706, 777), the author maintaining that all Vaubel's results can be explained by the presence of iron or of nitrite in the calcium hydroxide, the nitrite having been formed by the action of the air (compare this vol., ii, 320, 958). T. S. P.

The Solubility of Lead Sulphate and Lead Chromate. GEORG VON HEVESY and FRITZ PANETH (*Zeitsch. anorg. Chem.*, 1913, 82, 323—328).—Radium-*D*, being chemically inseparable from lead, may be used as an indicator in experiments with lead salts. The concentration of radium-*D* in the lead remains constant after mixture has once taken place, however small the quantity of the lead may be. A quantity of 10^{-10} grams of radium-*D* may be measured by means of an electroscope, using the β-radiation of radium-*E*, whilst by waiting until an equilibrium quantity of radium-*F* has formed, and using the α-radiation, the sensitiveness is increased to 10^{-12}.

The solubility of lead chromate is found by the former method to be 1.2×10^{-5} grams per litre at 25°. Kohlrausch's approximate estimate from the conductivity is 10^{-4}. This is the least soluble salt of lead. Lead sulphide gives the value 3×10^{-4} grams per litre in water, or 1.5×10^{-4} in presence of an excess of hydrogen sulphide, the higher value in the former case being due to partial hydrolysis.

The method of radioactive indicators has the advantage over methods involving the weighing of small quantities that there is no danger of the inclusion of impurities in the result. C. H. D.

Atomic Weight of Copper. WILLIAM ŒCHSNER DE CONINCK and F. DUCELLIEZ (*Rev. gen. Chim. pure Appl.*, 1913, 16, 122—123).—A determination of the atomic weight of copper. The metal was purified by the method described by Vigouroux (*Société des Sciences physiques et Naturelles de Bordeaux*, 1905-1906, 34), and the estimation carried out by conversion into the oxide; the mean of five experiments gave the atomic weight of copper as 63·549.

F. M. G. M.

The Action of Sulphides of the Allyl Group on Lead Amalgam and Mercury. MANINDRA NATH BANNERJEE (*Zeitsch. anorg. Chem.*, 1913, 83, 113—118).—Mercury is not completely purified from lead by distillation in a vacuum. The lead is completely removed from lead amalgam by rubbing repeatedly with

garlic juice, lead sulphide being formed, and this method is found to purify crude mercury completely. Some mercuric sulphide is also formed. The action of the garlic juice is due to the presence of sulphides of the allyl group. C. H. D.

Solubility of Mercury Haloids in Haloid Salt Solutions. WALTER HERZ and W. PAUL (*Zeitsch. anorg. Chem.*, 1913, 82, 431—437).—Determinations of the composition of a large number of saturated solutions of halogen salts of mercury and the alkali metals show a tendency to form complex salts, in which the molecular ratios are very simple. C. H. D.

Preparation of Mercury Derivatives of Aminosulphonic Acids which are Soluble in Water and Stable to Alkalis. KARL HOFMANN (D.R.-P., 261460).—The insolubility of the previously described mercury derivatives of aminosulphonic acids (Divers, T., 1896, **69**, 1634) detracts from their therapeutic value.

The *salt*, KO_3NSHg,H_2O, is prepared by treating an alkaline solution of aminosulphonic acid with mercuric oxide or chloride; the analogous *sodium* salt is crystalline, whilst the rubidium and lithium salts are also mentioned. F. M. G. M.

The Atomic Weight of Yttrium. II. RICHARD J. MEYER and M. WEINHEBER (*Ber.*, 1913, **46**, 2672—2675).—In a former communication (Meyer and Wuorinen, this vol., ii, 323) the atomic weight of yttrium was calculated from the ratio $Y_2O_3 : Y_2(SO_4)_3$, using 32 as the atomic weight of sulphur. Recalculation with correct atomic weights gives the atomic weight of yttrium as 88·71 and 88·73 respectively.

Fresh experiments on material which had been submitted to exhaustive fractionation by the iodate method gave the values 88·76, 88·80, and 88·73.

The authors have now determined the atomic weight from the ratio $Y_2(SO_4)_3 : Y_2O_3$, the yttrium sulphate, dehydrated at 400°, being transformed into the oxide by heating at a high temperature. The mean of six experiments gave 88·75 as the atomic weight of yttrium, the values obtained varying between 88·71 and 88·76.

As a mean of all experiments the atomic weight is taken to be 88·7. T. S. P.

Scandium in American Wolframite. HIRAM S. LUKENS (*J. Amer. Chem. Soc.*, 1913, **35**, 1470—1472).—The author has recovered pure scandium oxide from wolframite residues from the Zinnwald, using the method previously described by Meyer (A., 1909, ii, 45; 1910, ii, 853). The sulphate was prepared from the oxide and then re-converted into the oxide for the purpose of atomic-weight determinations. In two experiments the atomic weight of scandium was found to be 44·59 and 44·77 respectively.

The oxide was shown to be pure by spectral and radioactivity tests. T. S. P.

The Theory of the Preparation of Aluminium. RICHARD LORENZ, ASMUS JABS, and W. EITEL (*Zeitsch. anorg. Chem.*, 1913, **83**, 39—50. 328. Compare Pascal and Jouniaux, this vol., ii, 508; Puschin and Baskov, *ibid.*, 318; Fedotéev and Iljinsky, *ibid.*, 324). —The freezing-point curve of mixtures of cryolite and alumina is found to have a eutectic point at 33 mol. % Al_2O_3 and 937°. Solid solutions are formed up to 20 mol. % Al_2O_3, but not on the alumina side of the eutectic. Irregularities in the cooling curves are frequent, owing to the tendency to undercooling and the low thermal conductivity. Zonal structure is observed in the solid solutions under the microscope. On approaching the eutectic composition, marked segregation takes place, and needles of corundrum appear together with the crystallites of the solid solution. A definite eutectic structure is not obtained, but aggregate polarisation is observed in the ground mass.

The results obtained with cryolite and sodium fluoride differ somewhat from those of Fedotéev and Iljinsky, the eutectic point being found at 23 mol. % cryolite and 77 mol. % sodium fluoride at 886°. Solid solutions are formed on the sodium fluoride side.

C. H. D.

The Density of Aluminium. FRANCIS J. BRISLEE (*Trans. Faraday Soc.*, 1913, **9**, 162—173. Compare A., 1912, ii, 847).—Aluminium containing 0·36% of impurities has in the cast state D^{4} 2·703. Worked specimens of aluminium increase in density on annealing. With sheet metal containing 0·67% of impurities, the following values of D_4^{18} have been obtained: hard, 2·7076± 0·0002; annealed for two hours, 2·7086±0·0002; annealed for twenty-two hours, 2·7085±0·0001.

C. H. D.

Some Colloidal Solutions Derived from Hydrated Alumina. WILLIAM B. BENTLEY and R. PHILLIPS ROSE (*J. Amer. Chem. Soc.*, 1913, **35**, 1490—1499).—When freshly precipitated and well-washed aluminium hydroxide is dissolved to saturation in a hot 8% solution of acetic acid, a colloidal solution is obtained which is coagulated by the addition of hydrochloric acid; nitric acid will similarly produce coagulation, and also potassium sulphate, but not sulphuric acid. The acetic acid may be replaced by formic, propionic, or butyric acid, but the last two are much less effective.

The various experiments carried out by the authors lead them to the conclusion that the colloidal solution is one of a basic aluminium acetate and not of aluminium hydroxide. T. S. P.

The Constitution of Aluminates. WILLIAM BLUM (*J. Amer. Chem. Soc.*, 1913, **35**, 1499—1505).—The author has determined the changes in hydrion concentration taking place in a solution of aluminium chloride during the precipitation and re-solution of aluminium hydroxide by alkalis, by means of a hydrogen electrode (compare Hildebrand, this vol., ii, 721, 727). From the curves showing the relation between the *E.M.F.* and the number of c.c. of alkali added, the points at which precipitation of the aluminium

hydroxide begins and at which its re-solution is complete, can be determined, and the results indicate that one molecule of freshly-precipitated aluminium hydroxide dissolves in exactly one molecule of sodium or potassium hydroxide, that is, that an aluminate is formed of the composition $NaAlO_2$ or $KAlO_2$. This result disproves the conclusion of Mahin, Ingraham, and Stewart (this vol., ii, 139) that the solubility of aluminium hydroxide in bases is due principally to its colloidal properties, and not to the formation of salts.
T. S. P.

The Preparation of Aluminium Nitride from its Elements. JOHANNES WOLF (*Zeitsch. anorg. Chem.*, 1913, **83**, 159—162).—Preparation from fine aluminium by Fichter's method (A., 1907, ii, 691) having failed to give more than a small absorption of nitrogen, it was found that at a higher temperature, about 820°, a vigorous reaction set in, the product then containing 31·74% N, a quantity which was not further increased by powdering and heating for a short time in nitrogen, but after long heating rose to 32·55 (compare Fichter and Spengel, this vol., ii, 711). C. H. D.

Influence of Foreign Substances on the Crystal-form of Alum. PETR A. ZEMJATSCHENSKY (*Zeitsch. Kryst. Min.*, 1913, 52, 604—606; from *Mém. Acad. Sci. St. Pétersbourg*, [viii], 30, 1—19).—From solutions containing hydrochloric acid of varying concentration and at different temperatures crystals of alum sometimes present the form of the pentagonal dodecahedron (210). Under certain conditions the compounds

$$3(K_2Al_2S_4O_{16},24H_2O),K_2SO_4,8KCl,3Al_2Cl_6$$

and $2K_2SO_4,H_2SO_4,6H_2O$ also separate. L. J. S.

The Action of Hydroxyl Ions on Aluminium and Clayey Soils by Marling. PAUL ROHLAND (*Landw. Jahrb.*, 1913, 44, 437—440).—A continuation of previous work on the action of hydroxyl ions on clay soils, the changes being studied by the adsorption of compounds such as malachite-green or aniline-blue (compare this vol., ii, 27, 302, 356, 412). F. M. G. M.

Decomposition of Felspar and its Use in the Fixation of Atmospheric Nitrogen. WILLIAM H. ROSS (*J. Ind. Eng. Chem.*, 1913, **5**, 725—729).—Many processes have been patented relating to the decomposition of felspar with the object of rendering the potassium contained in it available as a plant food. Most of the methods depend on heating the substance to a high temperature, either alone or mixed with calcium oxide, calcium sulphate, etc. The author has carried out an investigation in order to ascertain the efficiency of ignited felspar in fixing nitrogen through the agency of the combined alumina or silica present, and finds that when a mixture of felspar, calcium oxide, and carbon is heated at 1400° for a few hours in an atmosphere of nitrogen, the felspar may absorb 7·44% of its weight of nitrogen; this quantity is greater than that which would be required to combine with the alumina

present to form aluminium nitride, but no direct experiments have been made to determine in what form the nitrogen is combined. The mixture evolves ammonia when boiled with water or sodium hydroxide solution. During the ignition at the temperature mentioned the whole of the potassium present in the felspar is volatilised. W. P. S.

Binary Systems of Manganous Chloride with the Chlorides of Some Alkali Metals. CARLO SANDONNINI and G. SCARPA (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 163—168).—The paper deals with the thermal analysis of the systems $LiCl-MnCl_2$, $NaCl-MnCl_2$, and $KCl-MnCl_2$. The results show that in this case also lithium chloride resembles magnesium chloride rather than the chlorides of the alkali metals in its behaviour. Lithium chloride and manganous chloride form solid solutions in all proportions; the curve shows a minimum at about 48 mol. % of LiCl and 555°.

Sodium chloride and manganous chloride form (at 441° and 445° respectively) two compounds which decompose on fusion, and probably have the compositions $NaCl,2MnCl_2$ and $4NaCl,MnCl_2$.

Potassium chloride and manganous chloride form two compounds. One, $KCl,MnCl_2$, has m. p. 495°. The other, $4KCl,MnCl_2$, is formed at 445°, and decomposes on fusion. The eutectic mixture of $KCl,MnCl_2$ and KCl lies at 35 mol. % of KCl and 450°. That of the two compounds lies at 65 mols. % of KCl and about 428°. The compound $4KCl,MnCl_2$ corresponds with the chloromanganokalite recently found in the minerals of Vesuvius. R. V. S.

Studies on Oxidation. III. The Oxidative and Catalytic Activity of Manganese Compounds. REGINALD T. COLGATE (*J. Soc. Chem. Ind.*, 1913, **32**, 893—898).—The interactions of manganese salts, hydrogen peroxide, and potassium permanganate have been studied, as well as the oxidation of hydrogen by permanganate. The results are held to indicate that manganese salts resemble ferrous salts in so far as they promote oxidation at all, a similar explanation (see this vol., ii, 967) being given of their oxyphoric and catalytic power. Hydrogen peroxide, however, is not powerful enough to convert the manganese salt into a perhydrol, permanganate being necessary; the permanganate acts as a depolariser, and is itself eventually reduced to the dioxide.

A similar explanation of the catalytic activity of manganese dioxide is given. It is assumed that this compound, in its hydrated form, is converted into a perhydrol, which is itself either so unstable that it is at once resolved into oxygen and a manganous compound, or else it gives rise by hydrolysis to hydrogen trioxide, which immediately decomposes.

A peroxide character is assigned to potassium permanganate, and it is argued that it always acts as an oxidising and not as a reducing agent. It is, however, not the immediate agent of oxidation, but acts as a hydrogen depolariser, the OH-ion of the electrolyte being the effective oxidising agent when it is used. The suggestion previously put forward (this vol., ii, 498) that hydrogen

peroxide may be a product of the oxidation process is withdrawn, although it is probable that hydrogen peroxide may be a product of hydrolysis. T. S. P.

Melting Points of Refractory Elements. I. Elements with Atomic Weight 48–59. GEORGE K. BURGESS and R. G. WALTENBERG (*Zeitsch. anorg. Chem.*, 1913, **82**, 361—372; and *J. Washington Acad. Sci.*, 1913, **3**, 371—378).—The determinations are made by means of the micropyrometer (Burgess, *Physikal. Zeitsch.*, 1913, **14**, 158), using minute particles of the metals on a platinum or iridium strip in an atmosphere of purified hydrogen. It is shown that an appreciable error is not introduced by the formation of alloys. The melting points of nickel (1452°) and palladium (1549°) are used for calibration. The following results are obtained: Iron (electrolytic or reduced by hydrogen), 1533±1°; cobalt (Kahlbaum), 1477±2°; chromium, 1520°; manganese (97·5%), 1254°, the value for pure manganese being perhaps 20° higher; vanadium, 1720±30°; titanium, 1795±15°.

Photo-micrographs are also given, showing the stages of the melting process. C. H. D.

A Specimen of Ancient Iron from Ceylon. WALTER ROSENHAIN (*Trans. Faraday Soc*, 1913, **9**, 132—135. Compare Hadfield, A., 1912, ii, 258).—A portion of a link from a chain, exposed to the air in Ceylon for two thousand years, was largely uncorroded. The iron had the structure of a somewhat porous wrought iron, and contained Si 0·138, S 0·054, P 0·223, Cu 0·076, and Ni 0·074%. In spite of the comparatively high sulphur content, the metal corroded very slowly, a result possibly connected with the simultaneous presence of copper and nickel. Manganese, chromium, molybdenum, and vanadium were absent. C. H. D.

Thermal Effects and Magnetic Changes of Ferromagnetic Substances at High Temperatures. KŌTARŌ HONDA (*Sci. Rep. Tōhoku Imp. Univ.*, 1913, [i], **2**, 69—94. Compare Honda and Tagaki, this vol., ii, 222).—The thermal method has now been made more sensitive, so that the thermal change accompanying the magnetic transformation may be recognised. The $\gamma \longrightarrow \alpha$ or $\beta \longrightarrow \alpha$ change in pure iron begins at about 800°, and the development of heat is still perceptible down to 700°. In nickel the thermal change extends from 375° down to about 250°. Cast cobalt gives a distinct development of heat, but after annealing this becomes less, and it almost disappears after repeated heating and cooling. The magnetic change also extends over a considerable range of temperature, which increases with increasing strength of field. The development of heat is independent of the strength of the magnetic field. At the eutectoid point the magnetic properties of steels change discontinuously.

The evidence favours the view that the supposed $\beta \longrightarrow \alpha$ change is not a phase change, but represents a change within a single phase. Similarly, nickel and cobalt are regarded as existing in one

modification only, which undergoes a magnetic change within an interval of temperature. The beginning of the magnetic change in steels on cooling is at 795—770°, and is independent of the carbon content. C. H. D.

An Electrolytic Theory of the Corrosion of Iron. BERTRAM LAMBERT (*Trans. Faraday Soc.*, 1913, **9**, 108—114. Compare T., 1910, 2426; 1912, 2056).—Oxygen acts in the corrosion of iron by destroying the hydrogen polarisation at the cathode. Iron which is sufficiently free from impurities to remain bright in water and air or in copper sulphate or nitrate reacts immediately in solutions of copper chloride. C. H. D.

The Oxidisability of Ferrosilicon. M. VON SCHWARTZ (*Zeitsch. anorg. Chem.*, 1913, **82**, 353—356).—The oxidation of ferrosilicon containing 50% Si is very slow in air at 850—1100°, the absorption of oxygen being incomplete after one hundred and twenty hours. In oxygen the reaction is more rapid, but is still far too slow for quantitative purposes. The material is used in fine powder. C. H. D.

Studies on Oxidation. II. The Nature of the Process in which Hydrogen Peroxide is Utilised. Iron Salts as Catalysts. C. S. MUMMERY (*J. Soc. Chem. Ind.*, 1913, **32**, 889—893. Compare this vol., ii, 498).—The author has studied the interaction of hydrogen peroxide with ferrous and ferric sulphates under different conditions, and also the oxidation of formic acid by hydrogen peroxide in the presence of iron salts. The results obtained are held to justify the conclusion that ferrous salts promote oxidation by means of hydrogen peroxide in virtue of the formation of a "perhydrol" of the type FeX(O·OH), which salt is formed reversibly, and is alternately produced from and reconverted into ferrous salt when an oxidisable substance is present together with hydrogen peroxide. Evidence for the formation of such a ferrous perhydrol is adduced from the fact that when hydrogen peroxide is added to ferrous sulphate in the presence of Trillat's agent (*pp'*-tetramethyldiaminodiphenylmethane) dissolved in citric acid, a brilliant blue colour is produced. The action does not take place, however, if the agent is added last, nor do ferric salts and hydrogen peroxide determine the appearance of the blue colour, but give rise to a brown colour instead of a blue.

The fact that ferric salts also promote oxidation may be accounted for by the formation of a ferric perhydrol, for example, $FeX_2(O{\cdot}OH)$. As, however, the ferric salts are less basic than ferrous salts, they give rise to a far smaller proportion of the perhydrol, and are consequently less active.

The catalytic decomposition of hydrogen peroxide by iron salts in the absence of an oxidisable substance is ascribed to the formation of higher perhydrols, which are regarded as derivatives of hydrogen trioxide.

The formation of the perhydrol converts the hydrogen peroxide

into an electrolyte, which can then act as an oxidiser, in accordance with the view expressed by E. F. and H. E. Armstrong (this vol., i, 1116) that "the catalyst may well be defined as the agent which brings about the inclusion of the interacting substances in the electrolytic circuit within which the change takes place so soon as the circuit is established, the electrolyte being the actual agent by which the change is affected." T. S. P.

The Thermal Dissociation of Cobaltammonias. WILHELM BILTZ (*Zeitsch. anorg. Chem.*, 1913, 83, 177—193).—When the thermal dissociation of the cobalt-ammonias is studied by either the statical or the dynamical method, equilibrium is only reached very slowly. Hexa-amminocobaltichloride is stable even when heated for one hundred hours at 193°, but rapidly loses $1NH_3$ at 216°. With large quantities or shorter time very incomplete dissociation is obtained. Some of the changes proceed slowly for several days, and then more rapidly, the temperature remaining constant, and the reactions are irreversible. In many cases reduction to the cobaltous condition occurs. Cobaltic salts in presence of cobaltous salts may be estimated by adding an excess of alkaline arsenite in an atmosphere of nitrogen and titrating the excess of arsenite. In the case of the cobaltichloride, the compound $CoCl_2,\frac{1}{2}NH_3$ is formed, but the phosphate decomposes according to the equation:

$$6[Co(NH_3)_6]PO_4 = 3CoP_2O_7 + 34NH_3 + 3H_2O + N_2.$$

C. H. D.

Ammonia Compounds of the Nickel Haloids. WILHELM BILTZ and BRUNO FETKENHEUER (*Zeitsch. anorg. Chem.*, 1913, 83, 163—176).—The isobars have been determined by passing ammonia over the substance in a combustion tube kept very exactly at a constant temperature until equilibrium is attained. The isotherms have been determined by heating the flask containing the substance in boiling aniline (179°) or thymol (230°), the flask being exhausted before heating, and the pressure read after heating for an hour. The weight of the substance then enables its composition to be calculated. The vapour-pressure curves have also been determined.

The hexa-ammines are best prepared in the wet way, compounds prepared by the action of ammonia gas on the anhydrous salts being very bulky. The curves show the compounds $NiCl_2,6NH_3$, $NiCl_2,2NH_3$, and $NiCl_2,NH_3$, this being bright yellow, easily distinguishable from anhydrous nickel chloride. The decomposition of the mono-ammine occurs at 373°. The bromide and iodide only form the hexa- and di-ammine.

The following heats of reaction have been found: $NiCl_2,6NH_3 \rightleftharpoons NiCl_2,2NH_3 + 4NH_3 = 16$ Cal.; $NiCl_2,2NH_3 \rightleftharpoons NiCl_2,NH_3 + NH_3 = 21·6$ Cal.; $NiCl_2,NH_3 \rightleftharpoons NiCl_2 + NH_3 = 24·2$ Cal.; $NiI_2,6NH_3 \rightleftharpoons NiI_2,2NH_3 + 4NH_3 = 18·3$ Cal. A comparison of these heats of reaction with those determined calorimetrically gives a good agreement (compare Ephraim, this vol., ii, 129, 130). C. H. D.

Two Double Salts of Molybdic Acid. M. K. ELIASCHEVITSCH (*Zeitsch. Kryst. Min.*, 1913, **52**, 630—632; from *Ann. Inst. Mines, St. Petersburg*, 1910, **2**, 345—351).—Descriptions are given, in Fedorov's nomenclature, of the monoclinic crystals of the potassium and ammonium cobalt salts $3K_2MoO_4,Co_2(MoO_4)_3,4MoO_3,10H_2O$ and $3Am_2MoO_4,Co_2(MoO_4)_3,4MoO_3,10H_2O$, prepared by N. S. Kurnakov.

L. J. S.

The Reduction of Tin Chlorides by Hydrogen, and a New Method of Reduction. FRIEDRICH MEYER and HANS KERSTEIN (*Ber.*, 1913, **46**, 2882—2887).—When the vapour of tin tetrachloride, mixed with hydrogen, is passed through a horizontal quartz tube heated at 1000°, stannous chloride is produced. Stannous chloride and hydrogen, under the same conditions, give only small quantities (traces) of tin. Experiments in a special apparatus showed that the reduction of the stannic chloride commences at 200°, and that of stannous chloride at 350°.

For further experiments the authors used an apparatus arranged on the principle of a reflux condenser. The lower part of a quartz tube, sealed at the bottom, could be heated in an upright electric furnace; the upper part acted as a cooler. Into the top of the tube were fitted narrower tubes through which hydrogen and a mixture of hydrogen and stannic chloride vapour could be introduced; there was also an exit tube for waste gases. When stannous chloride was used, it was placed at the bottom of the quartz tube before the narrower tubes were introduced. With this apparatus, under appropriate conditions of temperature, etc., both stannic and stannous chlorides could be reduced to tin, or stannic chloride to stannous chloride, in a practically quantitative manner.

T. S. P.

Working Up of Platinum Residues. D. J. DE JONG (*Chem. Weekblad*, 1913, **10**, 833—834).—To obtain platinum chloride free from potassium a concentrated hot alkaline solution of the residues is reduced with sodium formate, the platinum collected and ignited, dissolved in *aqua regia*, and the chloride recrystallised. A detailed account of the experimental conditions is given. A. J. W.

Platinoammine Compounds. LUDWIG RAMBERG (*Zeitsch. anorg. Chem.*, 1913, **83**, 33—38).—By adding sufficient ammonium chloride in the reaction between potassium platinochloride and ammonia, it is possible to prevent the replacement of chlorine by hydroxyl, and so obtain the pure chloro-compounds. The product obtained in such an experiment contains 85% of the compound $[Pt2NH_3]Cl_2$, the remainder being $[Pt4NH_3]PtCl_4$ and $[PtCl4NH_3]_2PtCl_4$. By dissolving in ammonia, filtering and evaporating, a white product, $PtCl_2,1NH_3,H_2O$, is obtained, which is converted into *trans*-platosoammine chloride by heating in a stream of air, first at 110° and then at 250—260°, until no more ammonia is expelled.

trans-Platosoammine iodide is best prepared from platinous iodide and ammonia, boiling until dissolved, and then blowing

steam through the solution to expel excess. A yield of 90–95% is thus obtained.

The *cis*- and *trans*-nitrites have also been obtained in a colourless form.

C. H. D.

Mineralogical Chemistry.

Marcasite Nodules from Podolia, Russia. N. S. WATITSCH (*Zeitsch. Kryst. Min.*, 1913, **52**, 634; from *Annuaire Géol. Min. Russie*, 1910, **12**, 16—19).—Nodular concretions of marcasite occur in the chalk-marl at Lyadava, govt. Podolia. Analysis gave: Fe, 47·67; S, 51·96; P_2O_5, trace; D 4·76. They weather to limonite, containing: Fe_2O_3, 62·47; Al_2O_3, 1·43; P_2O_5, 1·32; insol., 23·91; loss at 100°, 14·50; loss on ignition, 9·75; total, 98·83.

L. J. S.

Minerals of the Ore-deposits of Kerch and Taman, Crimea. SERGEI P. POPOV (*Zeitsch. Kryst. Min.*, 1913, **52**, 606—614; from *Travaux Mus. Géol. Pierre le Grand, Acad. Sci. St.-Pétersbourg*, 1910, **4**, 99—198).—A detailed description is given of the various minerals, and several analyses are given of brown iron-ore (limonite), siderite, anapaite (A., 1903, ii, 303), vivianite and its alteration products (paravivianite, kertschenite and oxykertschenite, A., 1906, ii, 236), and wad.

L. J. S.

Autunite of Lurisia. GABRIELE LINCIO (*Atti R. Accad. Sci. Torino*, 1913, **48**, 959—967).—The mineral has the composition:

P_2O_5.	UO_3.	CaO.	H_2O.	Gangue.	Total.
13·21	60·57	5·64	19·95	0·76	100·13

It crystallises in fluorescent tablets in the rhombic system, is feebly radioactive, and hence resembles the autunite of Autun.

R. V. S.

Barytes from Kerch, Crimea. A. A. KASCHINSKI (*Zeitsch. Kryst. Min.*, 1913, **52**, 624; from *Ann. Inst. Mines, St. Petersburg*, 1910, **2**, 251).—A specimen of yellowish radiating barytes, fungoid in external form, from a limonite mine, gave:

BaO.	SO_3.	SiO_2.	Al_2O_3, Fe_2O_3, Mn_2O_3.	CaO.	MgO.	Na_2O.	Ign.	Total.
63·35	34·21	0·19	0·16	0·74	0·08	0·22*	0·76	99·71†

* Including trace of K_2O. † Also traces of Cl and P.

L. J. S.

Chemical Investigation of Certain Minerals from Ceylon Gravel. III. GEORGEI P. TSCHERNIK (*Bull. Acad. Sci St. Pétersbourg*, 1913, 721—732. Compare this vol., ii, 421, 518).—Gravel from the Ratnapura district contains dark grey, somewhat oblong pebbles,

one side of which retains traces of crystalline form, and has a black colour. This mineral gives a conchoidal fracture with velvet-black colour and semi-metallic lustre, its streak being grey. It is brittle, but shows no sign of cleavage, and its hardness is almost identical with that of orthoclase. At the edges of thin fragments a faint reddish-brown light is transmitted. Analysis gave the percentage composition:

CaO.	Y_2O_3.	Ce_2O_3.	UO_2.	ThO_2.	FeO.	MnO.	Ta_2O_5.	Cb_2O_5.	H_2O.	SnO_2, WO_3 and Na_2O.	Total.
1·99	17·85	3·72	6·06	1·52	3·41	0·21	49·58	14·96	0·12	Traces	99·41

Calculation from these numbers gives the formula:

$$12(Y_2O_3,Ta_2O_5) + 2(Ce_2O_3,Ta_2O_5) + 3[(FeO)_3,Ta_2O_5] + 4[UO_2,(Cb_2O_5)_2] + ThO_2,(Cb_2O_5)_2 + 3[(CaO)_2,Ta_2O_5].$$

The mineral has therefore the chemical constitution of a modified yttrotantalite, although its physical properties resemble more closely those of the allied fergusonites.

The properties of the mineral are discussed in their relations to those of other yttrotantalites. T. H. P.

Olivine and Melilite Crystals from Furnace Slags. KARL BESZ and F. W. RÜSBERG (*Centr. Min.*, 1913, 625—634).—Crystals of a pure iron-olivine, Fe_2SiO_4 (fayalite), gave analysis I. A mangan-fayalite gave II, corresponding with $3Fe_2SiO_4,Mn_2SiO_4$. The sulphur shown in this analysis is due to the presence of fine, dusty enclosures of iron and manganese sulphides in the crystals. From analyses of another mangan-fayalite, rendered impure by enclosed spinel, the composition $5Fe_2SiO_4,Mn_2SiO_4$ is deduced. Analysis of the enclosed spinel corresponds with $3(Ca,Mg,Mn)O,2(Fe,Al)_2O_3$. Lime-olivines gave III and IV, corresponding with: $10Ca_2SiO_4,6(Fe,Mg)_2SiO_4,3Mn_2SiO_4$ and

$$3Ca_2SiO_4,2(Mg,Fe)_2SiO_4,Mn_2SiO_4$$

respectively, these both approximating to the double salt, Ca_2SiO_4,R''_2SiO_4:

	SiO_2.	Al_2O_3.	FeO.	MnO.	CaO.	MgO.	S.	Total.
I.	29·59	1·54	69·18	trace	—	—	trace	100·31
II.	27·79	0·39	51·90	17·44	0·88	—	1·45	99·85
III.	33·17	—	18·97	11·21	35·11	2·09	—	100·55
IV.	36·10	trace	4·89	11·81	32·68	15·15	—	100·68

The physical constants (density, crystal-angles, and a selection of the optical constants) of these crystallised materials are compared in the following table:

	D.	(110) : (1$\bar{1}$0).	(021) : (0$\bar{2}$1).	α(Na).	β(Na).	γ(Na).
I.	4·28	49°24′	98°35′	—	1·877	1·886
II.	4·25	49 22	98 37	1·805	1·836	1·846
III.	3·341	47 20	98 21	1·6749	1·7054	1·7105
IV.	3·190	47 5	98 8	—	—	—

Water-clear crystals of melilite gave analyses V (D 2·957) and VI; and the composition is expressed as a mixture of the alumin-

ous gehlenite molecule, $3R''O,R'''_2O_3,2SiO_2$, with the silicate $3R''O,2SiO_2$. The optical constants of these crystals were determined:

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.	Na_2O.	Total.
V.	39·84	4·34	0·12	—	2·30	35·03	10·20	4·37	2·01	99·21
VI.	42·39	1·09	—	1·30	4·38	38·10	12·16	—	—	100·42

L. J. S.

Wolkonskoite. FRANZ ANGEL (*Zeitsch. Kryst. Min.*, 1913, 52, 568—579).—This green, earthy mineral fills nests and veins in calcareous sandstones of Permian age in the governments of Perm and Vyatka, Russia. When placed in water, it absorbs water, and crumbles to scaly fragments, which are optically isotropic, D 2·337. Analyses are given of material from: I, Perm; and II, Echinovka (Perm?):

	SiO_2.	Cr_2O_3.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	H_2O. over 160°.	H_2O. below 160°.	Total.
I.	36·04	21·79	0·63	4·60	4·65	2·33	4·38	6·65	15·17	99·71
II.	37·14	22·77	4·33	2·13	3·46	2·77	4·09	7·38	15·53	99·60

Neglecting water lost below 160°, the formula is

$$(H_2,Mg,Fe,Ca)_3(Cr,Fe,Al)_2Si_3O_{12},$$

which is analogous to the garnet formula.

An artificial material, of similar colloidal nature, was prepared from a solution of sodium silicate and chromium chloride.

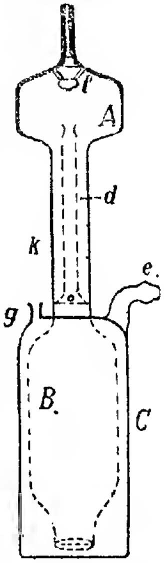
L. J. S.

A New Find of Alkaline Rocks in Timor. H. A. BROUWER (*Centr. Min*, 1913, 570—576).—Analyses are given of alkali-trachyte and shonkinite. L. J. S.

Weathering of Rock-forming Minerals under the Influence of Sulphurous Acid. H. LOTZ (*Jahrb. Min.*, 1913, ii, *Ref.* 180—183; from *Ber. Oberhess. Ges. Natur-Heilkunde, N.F. Naturw. Abt.*, 1910-11, 4, 70—108, and *Diss.*, Giessen, 1912).—Various rock-forming minerals were exposed to the action of a moist atmosphere containing air (80%), carbon dioxide (19%), and sulphur dioxide (1%). At the same time comparative experiments were made in an atmosphere of air 80% and carbon dioxide 20%. In the latter case there was little or no action, but in the presence of sulphur dioxide small amounts of the bases (especially alkalis, iron, and aluminium) passed into solution, with an enrichment of silica in the residue. Analyses are given of fourteen rock-forming minerals, and of the portions of each that passed into solution. L. J. S.

Analytical Chemistry.

Gas Analysis Apparatus. A. Lomschakow (*Chem. Zeit.*, 1913, **37**, 1262).—An apparatus for use in gas analysis consists of an absorption vessel *A* (see figure), and two reagent vessels, *B* and *C*. The reagent is introduced into *C* through the opening *g*, which is then closed by a rubber stopper; the vessel *B*, contained in *C*, is open at the bottom, and, by means of a rubber bulb attached to the opening *e*, the reagent may be caused to fill the vessel *A*. The gas under examination is allowed to enter by the capillary at the top of *A*, the reagent being driven back into *B* through the tube *d*, the quantity of solution contained in the space between the walls *d* and *k* passing through the small hole at the bottom of the tube *d*. After the gas has been introduced into the apparatus, the rubber bulb is compressed suddenly, causing a portion of the reagent solution to be expelled up the tube *d* against the plate *f*; this operation is repeated a few times in order to bring the solution in contact with the gas. The residual volume of gas is then driven back into the measuring burette by compressing the bulb, and causing the reagent solution to fill the vessel *A*. W. P. S.



General Remarks on Methods of Volumetric Analysis. M. Emmanuel Pozzi-Escot (*Bull. Assoc. chim. Sucr. Dist.*, 1913, **31**, 124–127).—The author advocates the use of normal solutions in volumetric estimations in preference to solutions which have been standardised empirically for one particular purpose. W. P. S.

Use of the Sense of Smell in Volumetric Estimations. Julius F. Sacher (*Chem. Zeit.*, 1913, **37**, 1222).—Substances possessing a strong smell, such as *iso*valeric acid, acetic acid, phenol, etc., and the salts of which are odourless, may be titrated without the use of any indicator other than the sense of smell, the disappearance of the odour on the addition of the alkali solution indicating the end-point of the titration. It is advisable, however, to add a slight excess of the alkali, and to titrate this excess with standard acid solution as the neutral point is indicated more sharply by the development of a slight odour than by its disappearance. Hydrolytic action and the action of carbon dioxide derived from the atmosphere influence the results to a certain extent. Similarly, ammonia can be titrated accurately. W. P. S.

An Automatic Pipette. C. H. McCharles (*J. Ind. Eng. Chem.*, 1913, **5**, 755—756).—The pipette is similar to that described by Smith (A., 1912, ii, 678), but differs in that the point to which the liquid rises in the capillary is constant. This is attained by having two stock bottles, one being placed higher than the other, and discharging into this through a siphon arrangement, which maintains a constant level of liquid in the lower reservoir from which the pipette is filled. W. P. S.

Estimation of Water of Crystallisation in Sulphates. Simon B. Kuzirian (*Amer. J. Sci.*, 1913, [iv], **36**, 401—405).—When sulphates are fused with sodium paratungstate, no decomposition of the sulphates occurs, reaction taking place in accordance with the equation: $M''SO_4 + Na_2O,12WO_3 = Na_2SO_4 + M''O,12WO_3$. It follows that the water of crystallisation in sulphates may be estimated by fusing them with an excess of the paratungstate. The method was tested on the hydrated sulphates of copper, aluminium, and nickel, and on chrome alum and potassium alum, and found to be quantitative. In these tests the loss in weight of the mixture was determined, and also the water expelled was collected and weighed. It is sufficient to keep the mixture in quiet fusion for fifteen to twenty minutes. T. S. P.

Estimation of Chlorine in the Blood. Ivar Bang (*Biochem. Zeitsch.*, 1913, **56**, 158).—A criticism of the method of Rogée and Fritsch (this vol., ii, 872). S. B. S.

Hydrolytic Action as a Source of Error in the Estimation of Iodine and Bromine in Mineral Waters and Saline Deposits. Paul Kaschinsky (*Zeitsch. angew. Chem.*, 1913, **26**, 492—494).—Magnesium bromide and magnesium iodide are decomposed by water with liberation of the halogen acids, and when the residue obtained on evaporating the water, etc., is heated over a flame, the whole of the iodine and almost all the bromine present may be lost. It is essential in this estimation to precipitate the magnesia by the addition of potassium hydroxide; after the magnesium hydroxide has been separated by filtration, the iodide and bromide are estimated in the usual way. Potassium hydroxide is to be preferred to calcium hydroxide for the removal of the magnesia, as potassium chloride is less soluble than calcium chloride in the alcohol used during the subsequent stages of the estimation. W. P. S.

The Action of Persulphates on Iodates and the Estimation of Periodates in Presence of Persulphates. Erich Müller and Walther Jacob (*Zeitsch. anorg. Chem.*, 1913, **82**, 308—314).—It is known that persulphates and iodates react to form sulphates and periodates, but an analytical method of determining how far the reaction proceeds has been lacking. The reaction $IO'_4 + 2I' + 2H^{\cdot} = IO'_3 + H_2O + I_2$ is quantitative in alkali hydrogen carbonate solution, but proceeds very slowly in alkali hydroxide solution.

When iodide is present, twice as much alkali hydrogen carbonate is added as is required to convert the hydroxide into carbonate, followed by arsenite solution and potassium iodide at 50°, and after cooling the solution is titrated with iodine solution. In this way periodate may be accurately estimated in presence of iodide. In presence of persulphate, however, low values are obtained, as the reaction $3IO'_4 + I' = 4IO'_3$, which does not occur at the ordinary temperature in alkali hydroxide solution, is accelerated by persulphates, hypoiodite being formed as an intermediate product.

A mixture containing only persulphate and periodate is made alkaline with alkali hydroxide, and potassium iodide is added. After boiling and cooling, the solution is acidified with sulphuric acid, and the iodine titrated with thiosulphate, giving the total periodate persulphate. Another portion is mixed with alkali hydroxide, and reduced by boiling with granulated zinc; after acidifying and adding iodate, the liberated iodine is titrated with arsenite in alkali hydrogen carbonate solution. This gives the periodate oxygen: $IO'_4 = I' + 4O$, and this is subtracted from the total previously obtained. The addition of alkali hydrogen carbonate must be performed in a reflux apparatus to avoid loss of iodine.

It has not been possible to find a reducing agent which acts on either persulphate or periodate, leaving the other intact.

C. H. D.

Volumetric Estimation of Fluorine. ALFRED GREEFF (*Ber.*, 1913, **46**, 2511—2513).—When ferric chloride is added to neutral aqueous solutions of the alkali fluorides, white, crystalline precipitates are formed having the general formula M_3FeF_6, analogous to that of cryolite; the *sodium* and *potassium ferrifluorides* were thus obtained. The existence of a double salt of the formula $2FeCl_3,2KF$ (Guyot, A., 1871, 854) could not be verified.

Sodium ferrifluoride is only very sparingly soluble in water, and does not give a red coloration with thiocyanates. If, however, ferric chloride is run into a solution of an alkali fluoride containing some potassium thiocyanate, excess of the ferric chloride is indicated not by the formation of a red, but by the formation of a yellow, colour. The colour change is not sharp, but can be made more evident by shaking the solution with a mixture of alcohol and ether, the ethereal layer then taking up the red colour of the ferric thiocyanate. The colour change is still not sharp enough for volumetric purposes, but can be made so by diminishing the slight solubility of the alkali ferrifluoride by the addition of sodium chloride. It is necessary that the aqueous solution of the fluoride used should be neutral to phenolphthalein.

The method of estimation is as follows: 0·5 Gram of the substance is dissolved in 25 c.c. of water, 20 grams of sodium chloride and 5 c.c. of potassium thiocyanate solution (1: 5) are added, and the solution titrated with standard ferric chloride solution until a weak yellow colour is obtained. Ten c.c. of alcohol and 10 c.c. of ether are then added, the solution is well shaken (in a corked

flask), and further titrated with ferric chloride until the red colour persists in the ethereal layer, even after a long time.

The method can be extended to the estimation of commercial sodium fluoride, which generally contains some acid fluoride NaF,HF, and also sodium silicofluoride. The hot solution is neutralised with standard alkali, using phenolphthalein as indicator, whereby the total quantity of acid fluoride and silicofluoride is obtained; the neutral solution is then titrated with ferric chloride as above. The quantity of acid fluoride present is determined by precipitating the silicofluoride as potassium silicofluoride by the addition of potassium chloride and alcohol, and then titrating with sodium hydroxide. Knowing the total quantity of acid fluoride and silicofluoride present, and also the quantity of acid fluoride, the amount of silicofluoride can be calculated. T. S. P.

Modification of Schulte's Apparatus for the Estimation of Sulphur in Iron and Steel. HANNS FISCHER (*Chem. Zeit.*, 1913, **37**, 1223).—In this method the iron or steel is heated in a flask with hydrochloric acid, and the gases evolved are passed into two absorption flasks containing water and cadmium-zinc acetate solution respectively. In order to prevent the contents of the absorption flasks flowing back into the decomposition flask when the latter is cooled at the end of the operation, two safety bulbs are attached to a side-tube on the delivery tube; the second of these bulbs is partly filled with water, and its outer limb is connected with a vertical tube. The second absorption flask may also be provided with a long, vertical tube, through which the non-absorbed gases may escape. W. P. S.

Fusion Method for the Estimation of Sulphur in Iron and Steel. FREDERICK H. FRANKLIN (*J. Ind. Eng. Chem.*, 1913, **5**, 839—842).—The following method is recommended: Three grams of the sample are dissolved in about 120 c.c. of copper-potassium chloride solution (prepared by dissolving 600 grams of copper-potassium chloride in warm water, adding 30 c.c. of hydrochloric acid and 30 c.c. of 20% barium chloride solution, and diluting the mixture to 1600 c.c.; it should be filtered after twenty-four hours); the insoluble residue is collected on an asbestos filter, washed with dilute hydrochloric acid, and then with water. The residue is separated as far as possible from the asbestos, dried at a temperature slightly under 100°, and then fused with a mixture of 3 grams each of sodium carbonate and sodium peroxide. When cold, the mass is dissolved in hydrochloric acid, the solution is evaporated to dryness, and the residue is treated with water containing a small quantity of hydrochloric acid. The solution is filtered to remove silica, and the sulphuric acid in the filtrate is then precipitated as barium sulphate in the usual way. W. P. S.

Estimation of Sulphur in Pyrites and Other Sulphides. MAX DITTRICH (*Zeitsch. anorg. Chem.*, 1913, **83**, 27—32).—The method of Heczko (A., 1911, ii, 89, 296) may be modified with

advantage by providing the transparent silica tube with ground-on silica connecting tubes, the joints being lubricated with graphite. The escaping gases pass through a long series of absorbing bulbs, containing bromine and bromine water. The finely powdered ore is heated in a porcelain boat. The final heating of the boat, after most of the sulphur dioxide has been driven over, is performed by means of a Teclu burner. The sulphur is estimated as barium sulphate in the usual way. The residue in the boat, which is used for further analysis, should be tested for sulphates. Satisfactory results are readily obtained with pyrites, but zinc sulphide requires very fine powdering, and heating in a long boat to expose a large surface, otherwise sulphur is retained.

Jannasch's method of heating in a stream of oxygen or carbon dioxide laden with bromine, the sulphur being expelled as sulphur bromide, is also successful, but when arsenic, antimony, or other metals forming volatile bromides are used, the exit tube must be wide to avoid stoppage. C. H. D.

Estimation of Sulphur in Pyrites Residues. L. Sznajder (*Chem. Zeit.*, 1913, **37**, 1107).—The following volumetric method is proposed: A quantity of 2·5 grams of the sample is heated to redness for thirty minutes with 5 grams of a mixture of sodium carbonate and zinc oxide; after cooling, the mixture is taken up with water, diluted to 250 c.c., and filtered. Two hundred c.c. of the filtrate are heated to boiling, phenolphthalein is added, and dilute hydrochloric acid is run in until the red coloration disappears. Thirty c.c. of $N/5$-barium chloride solution are now added to the hot solution, which is then titrated with $N/5$-sodium carbonate solution. The percentage quantity of sulphur is found from the equation $S=0·16(30-a)$, a being the number of c.c. of $N/5$-sodium carbonate solution required for the titration.

W. P. S.

Estimation of Sulphur in Organic Compounds. Hermann Apitzsch (*Zeitsch. angew. Chem.*, 1913, **26**, 503—504).—A piece of combustion tube is drawn out at one end, the narrow tubing so formed opening into an absorption apparatus containing sodium hypobromite solution. The substance containing sulphur is weighed into a porcelain boat and placed in the tube, and on both sides of the boat are placed special spirals of platinum gauze. The substance is burned in a current of oxygen, the platinum acting as a catalytic agent, and the products of combustion collected in the absorbent. When the combustion is complete, the tube is washed out, the washings added to the sodium hypobromite solution, and the sulphur precipitated as sulphate in the usual way. Volatile substances are vaporised outside, and passed through the tube according to the usual method.

The method is accurate, and preferable to the Carius method.

T. S. P.

Estimation of Sulphur in Caoutchouc. Ernst Deussen (*Zeitsch. angew. Chem.*, 1913, **26**, 494—496).—The method described

previously by the author (A., 1910, ii, 750) for the detection of sulphur in organic compounds may be applied to the estimation of sulphur in caoutchouc. The substance is oxidised by repeated evaporation with nitric acid; the residue is then mixed with sodium carbonate, and ignited as described (*loc. cit.*). The sulphide which is obtained in solution on treating the fused mass with water is estimated colorimetrically by comparison with standard solutions prepared by reducing known quantities of sodium sulphate in a similar manner. Alkaline lead acetate solution is employed as the reagent in the colorimetric estimation. W. P. S.

Estimation of Free Anhydride Contained in Fuming Sulphuric Acid by Titration and Determination of Density. P. GAVELLE (*Mon. Sci.*, 1913, 3, I, 301—308).—A description of two methods for the estimation of sulphur trioxide (by titration) in fuming sulphuric acid; also an account of the determination of the densities at 20° of acids containing 0—30% of sulphur trioxide; the results are tabulated, and a formula for calculating the composition of the acids deduced. F. M. G. M.

Estimation of Ammonia and Nitrogen. HEINRICH HOLTKAMP (*Zeitsch. angew. Chem.*, 1913, **26**, 600).—A simple apparatus is described for the estimation of ammonia by the distillation method. The ordinary bulb trap above the distillation flask is replaced by a wide tube bent in the shape of a swan's neck. This connects, by means of a narrow tube, with a wide vertical tube opening into the absorbent standard acid. T. S. P.

Quantitative Ammonia Distillation by Aeration for Kjeldahl, Urea, and Other Nitrogen Estimations. III. PHILIP A. KOBER and SARA S. GRAVES (*J. Amer. Chem. Soc.*, 1913, 35, 1594—1604. Compare Kober, A., 1910, ii, 651; 1908, ii, 776).—An account of the process described earlier (A., 1908, ii, 776) with a discussion of the theory of the process, and with details of the method. Some additional directions as to manipulation are given, and also the results of experiments proving the trustworthiness of the process. D. F. T.

Colorimetric Estimation of Nitric Acid in Water. J. SIBER (*Zeitsch. Nahr. Genussm.*, 1913, **26**, 282—286).—The phenolsulphonic acid method of Grandval and Lajoux is recommended; the author finds that nitrites do not affect the results obtained, but that, when a large quantity of chloride is present, the water must be treated previously with silver sulphate. The minimum quantity of nitric acid (N_2O_5) which can be estimated by the process is about 0·02 mg. per 50 c.c. of water; when more than 3·0 mg. per 50 c.c. is present the colour comparison is difficult. The author employs a set of comparison tubes, prepared with known amounts of nitric acid, in the estimation (compare A., 1910, ii, 652). W. P. S.

Detection of Nitrous Acid in Presence of Nitric Acid. ANDRÉ LECLÈRE (*J. Pharm. Chim.*, 1913, [vii], 8, 299).—The test depends on the fact that nitrous acid is liberated from its salts by

citric acid whilst nitric acid is not. The liquid under examination is mixed with its own volume of a syrupy, aqueous solution of citric acid; on this mixture is superposed by means of a pipette a ½ or 1 % solution of ferrous ammonium sulphate. If nitrites are present in the liquid a brown ring appears at the surface of contact of the two solutions. If sulphides are present they should first be removed by adding zinc acetate to the solution, the test being then applied to the filtrate. T. A. H.

Nitrates and Nitrites in Milk. GEORGE D. ELSDON and JOHN A. L. SUTCLIFFE (*Analyst*, 1913, **38**, 450—454).—Nitrates have been added to milk as a preservative and to remove any turnip-like taste, whilst nitrites have been added with the object of obscuring the usual tests for formaldehyde when the latter has been introduced into the milk. Since the diphenylamine-sulphuric acid test gives a reaction with both nitrates and nitrites it is not applicable to the detection of nitrates or nitrites in the presence of each other, and, further, is too sensitive for use where relatively large quantities of nitrate are concerned. The brucine-sulphuric acid method is recommended for the purpose. In the absence of nitrites the serum obtained from the milk is treated with the reagent, and the coloration obtained is compared with that produced by known quantities of nitrate. In the presence of nitrites the coloration is produced immediately on the addition of the reagent, and then fades quickly to a certain extent. The bleaching action is independent of the amount of nitrite present, and the comparison solutions are prepared with the addition of 10 parts per 100,000 of sodium nitrite, the comparisons being made after the lapse of three hours. The authors find that potassium nitrate is reduced to nitrite in milk, the quantity of nitrite formed reaching a maximum in about four days, and then decreasing. The Griess-Ilosvay reagent is recommended for the detection and estimation of nitrites. Nitrites act as preservatives when added to milk, but nitrates are inefficient in this respect. W. P. S.

Estimation of Phosphorus in Vanadium Steel and Ferro-Vanadium. C. F. SIDENER and P. M. SKARTVEDT (*J. Ind. Eng. Chem.*, 1913, **5**, 838—839).—The sample is dissolved in dilute nitric acid, a small quantity of hydrochloric acid being added if necessary, the solution is evaporated to dryness, and the residue is baked until the ferric nitrate is decomposed. The residue is now dissolved in hydrochloric acid, 0·02 gram of aluminium in the form of aluminium chloride is added, the solution is nearly neutralised with ammonia, heated to boiling, and reduced by the addition of an excess of ammonium hydrogen sulphite. Phenylhydrazine is then added; if no precipitate forms, a few drops of ammonia are added, and then more phenylhydrazine. The precipitate obtained is collected, washed with hot water, and dissolved in nitric acid. This solution is treated with hydrogen peroxide and sodium carbonate, boiled, and the aluminium phosphate is precipitated by the addition of nitric acid until the solution is practically neutral to turmeric paper. The precipitate is collected, washed with ammon-

ium nitrate solution, dissolved in nitric acid, and a small quantity of hydrogen peroxide is added. If a pink or red coloration is produced, owing to the presence of vanadium, the precipitation with sodium carbonate and nitric acid must be repeated. The nitric acid solution of the precipitate is then treated with molybdate solution, and the phosphoric acid estimated in the usual way.

W. P. S.

Estimation of Total Phosphoric Acid in Soils. HERMANN FISCHER (*Bied. Zentr.*, 1913, **42**, 585—586; from *Internat. Mitt. Bodenkunde*, 1912, **2**, 541).—The soil (5—10 grams) is treated with about 50 c.c. of aqua regia, and kept covered until evolution of gas nearly ceases, after which it is evaporated to dryness. The residue is ignited, and again treated with the same amount of aqua regia, and evaporated to dryness. Strong nitric acid is added, and then evaporated until the hydrochloric acid is removed, and the residue is extracted with 5 c.c. of nitric acid and hot water. The filtrate, or an aliquot portion, according to the amount of phosphoric acid present, is evaporated down to 25 c.c., and the phosphoric acid estimated by Mitscherlich's method.

The potassium sodium carbonate method is inconvenient when as much as 5 grams of soil is used, owing to the large amounts of salts in the solution; and with less than 5 grams of soil it is difficult to obtain an exact average sample. N. H. J. M.

The Method of Combustion Calorimetry, and Elementary Analysis by means of the Calorimetric Bomb. M. DIAKOW (*Biochem. Zeitsch.*, 1913, **55**, 116—123).—Attention is called to the difficulties of the correct estimation of nitric acid formed in the combustion. A colorimetric method for the estimation of this acid by means of diphenylamine was not found satisfactory, and the Jodlbauer method was therefore employed. A method is described for estimating the carbon dioxide formed, and the oxygen used during combustion. The amount of oxygen compressed into the bomb is estimated by direct weighing, and from the analysis of this gas (which contains some argon, nitrogen, and carbon dioxide) and of the air, the initial composition of the compressed gaseous contents of the bomb can be found. After the combustion, the gaseous products are passed over adsorption bulbs containing soda-lime, and the carbon dioxide is estimated by weighing. Between the adsorption apparatus and the bomb, however, a T-piece is interposed, leading to a mercury bulb, in which a measured sample of the gas is collected, in which is estimated the carbon dioxide, oxygen, and nitrogen. From this analysis, and the relative amounts of carbon dioxide in this sample to that collected in the absorption bulbs, the amounts of nitrogen and oxygen in the bomb after combustion can be calculated. Correction in estimating the nitrogen must be made, due to the nitric acid formed, which is estimated by Jodlbauer's method.

NATHAN ZUNTZ, in an appended note (*ibid.*, 122), calls attention to the fact that correction must also be made for the argon contained in the commercial oxygen. S. B. S.

Cerium Dioxide as Contact Substance for the Combustion of Organic Substances. JULIUS BEKK (*Ber.*, 1913, **46**, 2574—2579).—Platinised asbestos, as used by Dennstedt, may be replaced with advantage, by asbestos impregnated with cerium dioxide, prepared by soaking the material in a solution of cerium nitrate and igniting. A layer of about 30 cm. is used in an ordinary combustion tube, and heated to a dull red heat, either in the common form of furnace or in one of the Dennstedt pattern. The substance is placed in a narrow tube, which is drawn out to a jet at the end nearest to the oxygen inlet, whilst the use of a short layer of lead peroxide is recommended in the case of nitrogen or sulphur compounds. As in Dennstedt's process, halogens may be estimated by the increase in weight suffered by a silver spiral or layer of molecular silver. The combustion is complete in fifteen to twenty minutes. Unlike platinised asbestos, the catalyst is not "poisoned" by sulphur dioxide, arsenious acid, or lead peroxide. J. C. W.

The Calorimetric Estimation of Ash. FRITZ (EDLER) VON KOSEK-NORWALL (*Chem. Zeit.*, 1913, **37**, 1181—1182).—It is well known that the weight of the ash from a coal burned in a bomb calorimeter may be 4—5% less than the weight obtained in the usual way by ashing the coal in the air in a platinum crucible; also, the weight of the ash may vary considerably in consecutive calorimetric determinations. These differences are only partly due to the fact that some of the ash is blown out of the crucible during the combustion in the calorimeter.

The author finds that the chief cause of these differences is the sulphur-content of the coal. During the combustion in the bomb sulphur trioxide is formed, and gives rise to soluble sulphates by combination with the alkalis, alkaline earths, and iron oxides contained in the ash; these sulphates dissolve in the water in the bomb, and are thus lost in the estimation of the ash. If, now, the contents of the bomb are washed out carefully, the boiling solution neutralised with sodium hydroxide in the presence of phenolphthalein as indicator, a yellowish-white precipitate is obtained, which may be collected, dried, and ashed in the usual way. If the weight of this ash is added to the weight of the calorimetric ash, the differences between consecutive estimations disappear, and the difference between the calorimetric ash and that estimated in the usual way is reduced to 1—1·5%. This remaining difference is probably due to the alkali content of the coal, which remains as soluble sulphates in the wash water, and is lost. T. S. P.

The Electrolysis of Potassium Chloride. HIRAM STANHOPE LUKENS (*J. Amer. Chem. Soc.*, 1913, **35**, 1472—1482).—In the electrolytic estimation of anions, using the Hildebrand cell, only small quantities of salt can be used. The author has investigated the accuracy which is attainable when solutions of potassium chloride containing 1—2 grams of potassium chloride are electrolysed.

It was found that the chief error was caused by the anolyte

creeping into the catholyte under the glass partition cup separating the anolyte and catholyte, owing to the fact that the glass is not wetted by the mercury. This could be prevented by platinising the bottom edge and outside of the cup, and then depositing a heavy coating of silver on the platinum. There was still a slight error caused by some decomposition of the amalgam occurring in the inner cell. This was obviated by cutting a section, 8 mm. in height, from the bottom of a beaker 40 mm. in diameter; this was cemented in an inverted position in the centre of the crystallising dish containing the mercury. When the glass cup was then placed in position, the mercury in the anode portion of the cell was confined to an annular space, about 10 mm. wide, between the cup and the section from the beaker, whereby the amalgam was formed close to the outer vessel, into which it quickly made its way and was decomposed.

The results obtained with this apparatus were very accurate, the errors being of the order of 0·0001—0·0003 gram on 0·6 gram of chlorine. 1·09 Grams of potassium chloride could be decomposed in an hour, using 1·6—2 amperes at 6·5—7 volts. T. S. P.

Blacher's Method of Estimating the Hardness of Water. W. HERBIG (*Färberzeitung*, 1913, **24**, 98—101, 113—114).—A discussion on various methods employed for estimating hardness in water. The author confirms the experiments of Blacher, Jacoby, and Koerber (*Zeitsch. angew. Chem.*, 1909, **22**, 967), in which stearic acid is employed, and describes modifications which he considers give more satisfactory results, which are demonstrated in tabular form. F. M. G. M.

Analysis of Alloys of Lead, Tin, Antimony, and Copper. D. J. DEMOREST (*J. Ind. Eng. Chem.*, 1913, **5**, 842—843).—Alloys consisting of these four metals may be analysed by heating the finely divided sample with concentrated sulphuric acid until the lead has been converted into sulphate, and the other metals have dissolved. The lead sulphate is collected and weighed, and the antimony in the filtrate is titrated with potassium permanganate solution. After the titration, the tin is reduced by means of iron in the presence of the antimony, and the stannous salt is titrated with iodine solution. Another portion of the sample is treated with sulphuric acid as before, the lead sulphate is separated, and the copper is precipitated as cuprous thiocyanate either with or without previous titration of the antimony. The cuprous thiocyanate may be titrated with potassium permanganate solution, or the copper estimated by the iodide method after the precipitate has been ignited and the copper oxide dissolved in nitric acid. Full details as to manipulation are given in the original. W. P. S.

Electrolysis of Nitric Acid Solutions of Copper. JOHN H. STANSBIE (*Trans. Faraday Soc.*, 1913, **9**, 11—13).—More complete deposition of copper from nitric acid solutions is obtained with a rotating than with a stationary cathode, as in the latter case

nitrous acid may accumulate at the surface of the metal. The addition of sulphuric acid is of advantage in securing complete deposition. When the rotation is stopped, the cathode should be washed before breaking the current. C. H. D.

Electrolytic Estimation of Copper in Solutions containing Nitric Acid. ELIZABETH GILCHRIST and ALEXANDER C. CUMMING (*Trans. Faraday Soc.*, 1913, **9**, 186—187).—The deposition of copper is complete, even in presence of a large excess of nitric acid, if carbamide is added to destroy nitrous acid. C. H. D.

New Method for the Electrolytic Analysis of White Metals for Bearings. I. COMPAGNO (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 221—226).—These alloys contain tin, antimony, and copper, together with lead, arsenic, iron, zinc, nickel, etc., as impurities. The method here described is said to be more exact as well as more rapid than those at present in use. The alloy (1 gram) is treated with 20 c.c. of nitric acid (D 1·4), first for some hours at the ordinary temperature, then for thirty minutes on the boiling water-bath; the tin and antimony then remain undissolved in the form of metastannic and metantimonic acids (which include also a little copper nitrate). After filtration, the copper and, if necessary, the lead are determined electrolytically, and in the remaining solution the other metals may be estimated if required. The precipitate of metastannic and metantimonic acids is then dissolved as directed in a previous paper (A., 1912, ii, 810), and electrolysed as there described. The deposited antimony and copper are weighed together, and the copper present is estimated as follows. The deposit is treated in the warm with 10 c.c. of dilute nitric acid (1 : 2) and 0 3 gram of tartaric acid; the solution is evaporated to dryness, redissolved in 20 c.c. of water, made alkaline with sodium hydroxide, and treated with 1—2 c.c. of potassium sodium tartrate solution (10%), and with about 0·3 gram of dextrose. After boiling, the cuprous oxide is dissolved in nitric acid, and the copper in the solution estimated (after addition of 2 c.c. of concentrated sulphuric acid) electrolytically. The liquid from which the antimony and copper have been removed is heated almost to boiling, and treated very cautiously with 120 c.c. of hydrochloric acid (D 1·19). Boiling is continued until the tin sulphide at first precipitated is entirely decomposed, and the liquid is then concentrated and heated for a few minutes with a few drops of hydrogen peroxide. After addition of 20 grams of pure oxalic acid and dilution to 500 c.c., the tin is deposited electrolytically, preferably in an apparatus described, which is especially adapted for operations in the warm with rotating electrodes. R. V. S.

Estimation of Small Quantities of Mercury in Organic Substances. SVENN LOMHOLT and J. A. CHRISTIANSEN (*Biochem. Zeitsch.*, 1913, **55**, 216—223).—The organic material is first destroyed in the presence of sulphuric or nitric acid and potassium per-

manganate. A small amount of copper sulphate is then added, and the copper and mercury are precipitated together by hydrogen sulphide. The sulphide is filtered off on to a Gooch crucible, and dissolved in a mixture of 5 c.c. of concentrated nitric acid and 1·5 c.c. of 1% hydrochloric acid. (This ratio of acids must not be departed from.) From the solution thus obtained, the mercury is separated by electrolysis after dilution to 40 c.c., using platinum wire for an anode, and a gold plate for cathode and a tension of 1·5 volts. After eight hours, the cathode is removed, dried, and weighed. It is then heated in a current of hydrogen to volatilise the mercury, and weighed again. The difference gives the amount of mercury. S. B. S

The Chemical Investigation of Aluminium. J. Czochralski (*Zeitsch. angew. Chem*, 1913, **26**, 501—503).—The analysis of aluminium, and of alloys rich in aluminium, is best carried out as follows. Two grams of borings are dissolved in a mixture of 40 c.c. of water, 40 c.c. of concentrated sulphuric acid, and 2 c.c. of nitric acid (D 1·48). The solution is diluted to 300 c.c., and warmed for some time at 80° in order to make the silicic acid ball together, after which the undissolved matter is collected, dried, and weighed. The residue is tested for purity with hydrofluoric and sulphuric acid, and if large it is fused with sodium carbonate–sulphur mixture, and further investigated for tin, antimony, and lead. If arsenic, bismuth, etc., are to be estimated in the filtrate, they are precipitated with hydrogen sulphide, otherwise the copper, and any traces of lead, are estimated electrolytically. To the filtrate from the metals of the hydrogen sulphide group are then added 20 grams of ammonium tartrate dissolved in 100 c.c. of water, the solution is made alkaline, and the iron, nickel, manganese, and zinc precipitated with ammonium sulphide; magnesium is precipitated from the filtrate as magnesium ammonium phosphate. The iron, nickel, etc., are separated in the usual way, the nickel and zinc being estimated electrolytically.

Special methods are described for the estimation of any particular impurity which may be present.

Microphotographs are given of aluminium containing impurities and of aluminium alloys. T. S. P.

The Increase in the Oxidising Potential of Dichromate Ion on Platinum caused by Certain Reducing Agents. An Improved Method for the Electrometric Titration of Ferrous Salts. George S. Forbes and Edward Payson Bartlett (*J. Amer. Chem. Soc.*, 1913, **35**, 1527—1538).—It is found that certain reducing agents, as, for example, ferrous sulphate, arsenious acid, chromous sulphate, and potassium ferrocyanide, increase the oxidising potential of the dichromate ion on platinum by amounts up to 0·2 volt. No other oxidising agent has been found to give a similar effect.

The potential increases continuously up to the point where all the dichromate is reduced, and then drops suddenly when excess

of the reducing agent is added. An excess of one drop of a 0·1N-solution of the reducing agent often depresses the potential by 0·5 volt, so that the method can be used for titrating a dichromate solution with a ferrous salt; the end-point reaction is much more delicate than with the ferrocyanide indicator.

The duration of the effect varies with the reducing agent used, from a few seconds to many hours; chlorides are fatal to the permanency, owing apparently to a side-reaction.

The authors suppose that the phenomenon is catalytic in nature, but direct tests of their hypothesis could not be devised.

T. S. P.

Estimation of Cobalt and Uranium in Steel. Heinrich König (*Chem. Zeit.*, 1913, **37**, 1106—1107).—The estimation of cobalt in steel entails a separation of this metal from nickel, as the two are always present together. The iron, nickel, and cobalt are first estimated electrolytically from an ammonium oxalate solution; the iron and nickel are then estimated separately, and the quantity of cobalt is found by difference. For the estimation of the nickel, the hydrochloric acid solution of the steel, after the removal of tungstic acid, is shaken with ether to separate the greater part of the iron. The acid solution is then heated to expel the ether, the iron is reduced by the addition of sulphurous acid, and the solution is neutralised with alkali solution. Potassium cyanide is now added, the separated chromium precipitate is removed by filtration, and the filtrate is boiled. The cobalt is thus converted into the complex potassium cobalticyanide, which remains in solution when the nickel is precipitated as hydroxide by the addition of potassium hydroxide and bromine. The nickel hydroxide is then collected, dissolved in hydrochloric acid, and the nickel estimated by the dimethylglyoxime method. The uranium is estimated as follows: The hydrochloric acid solution of the steel, after the removal of tungstic acid, is evaporated with sulphuric acid, the solution is diluted with water, nearly neutralised with ammonia, and the iron is electrolytically deposited from an ammonium oxalate solution. The electrolysis is continued until the ammonium oxalate has been converted into carbonate, and a precipitate consisting of the chromates, vanadates, and hydroxides of uranium, aluminium, and manganese is obtained. The uranium is, however, precipitated completely only when the ammonium carbonate has been decomposed by boiling the solution. When this has been done, the precipitate is collected, washed with dilute ammonium chloride solution, dissolved in hydrochloric acid, chromates are reduced by the addition of a few drops of alcohol, and the solution is oxidised with nitric acid. After iron, chromium, manganese, and aluminium have been precipitated by the addition of ammonium carbonate and sulphide, the solution containing the uranium and vanadium is acidified with acetic acid, boiled, and the vanadium sulphide removed by filtration. The filtrate is oxidised with nitric acid, and the uranium is precipitated by the addition of ammonia; the precipitate is washed with ammonium

chloride solution, ignited in a current of hydrogen, and weighed as UO_2. W. P. S.

Action of an Excess of a Soluble Ferrocyanide on Solutions of Zinc, Copper, and Nickel, and the Volumetric Estimation of the Latter. Raoul Meurice (*Ann. Chim. anal.*, 1913, 18, 342—345).—When zinc salts are treated in solution with an excess of potassium ferrocyanide, the precipitate obtained has the formula $Zn_3K_2[Fe(CN)_6]_2$, and its formation may be utilised as a means of estimating zinc volumetrically. The zinc solution is treated with an excess of standard potassium ferrocyanide solution, and the excess of the latter is then titrated with permanganate solution in a portion of the clear solution after the addition of sulphuric acid. In the case of copper salts, the ferrocyanide formed varies in composition with the concentration of the solution, and is slightly soluble; the ferrocyanide method cannot, therefore, be used for the volumetric estimation of copper. Nickel yields a definite ferrocyanide in the presence of an excess of potassium ferrocyanide and ammonium sulphate. For the estimation of this metal the solution (containing about 0·1 gram of the metal) is treated with 100 c.c. of 3·5% potassium ferrocyanide solution, 5 grams of ammonium sulphate are added, and the mixture is diluted to 200 c.c. After filtration, 100 c.c. of the filtrate are diluted to about 800 c.c., acidified with sulphuric acid, and titrated with permanganate solution. The potassium ferrocyanide solution is standardised against the permanganate solution, and this in turn against sodium oxalate; the iron equivalent of the permanganate is thus obtained, and 1 atom of iron is equivalent to 1 atom of nickel. W. P. S.

Detection of Potassium Dichromate in Milk. B. Grewing (*Zeitsch. Nahr. Genussm.*, 1913, **26**, 287).—Ten c.c. of the milk are mixed with 4 c.c. of a 3% aniline solution, and the mixture is allowed to flow on to the surface of 3 c.c. of concentrated sulphuric acid. A blue-coloured zone appears at the junction of the liquids if the milk contains dichromate. The test will detect as little as 0·01 gram of dichromate per litre, but in this case the colour obtained is reddish-violet, and does not develop until after the lapse of about eight minutes. Nitrates, formaldehyde, and hydrogen peroxide do not interfere with the reaction. W. P. S.

Colorimetric Estimation of Titanium in Iron and Steel. Charles R. McCabe (*J. Ind. Eng. Chem.*, 1913, 5, 735—736).—Two grams of the sample and 2 grams of non-titanium steel are dissolved separately in dilute sulphuric acid, and the solutions are oxidised with nitric acid. The solutions are now transferred to graduated tubes, diluted to the same volume, and compared. Having obtained solutions showing the same colour in equal volumes, hydrogen peroxide is added to each tube, and if any deepening of colour is observed in the solution of the sample, standard titanium solution is added to the other tube until the

tints are equal. When the iron or steel contains less than 0·02% of titanium the oxidised hydrochloric acid solution of both the sample and the non-titanium steel are extracted with ether to remove the greater part of the iron; the acid solutions are then boiled, ammonia is added, the precipitates are collected, dissolved in sulphuric acid, and the titanium is estimated by comparison, as described previously. W. P. S.

Estimation of Vanadium in Steel by the Hydrogen Peroxide Colorimetric Method. CHARLES R. MCCABE (*J. Ind. Eng. Chem.*, 1913, **5**, 736—737).—The method consists in treating a non-vanadium steel in precisely the same way as the sample, the colour of the latter solution being then imitated by the addition of a standard vanadium solution to the non-vanadium steel solution, the final comparison being made at equal volumes. Two grams each of the sample and a non-vanadium steel are dissolved in 40 c.c. of nitric acid, D 1·2, 0·1 gram of potassium permanganate is added to each solution, and, after two minutes' heating, the solutions are clarified by the addition of ammonium hydrogen sulphite. Excess of sulphur dioxide is expelled by heating, and the colours of the solutions are then matched. One c.c. of a 3% hydrogen peroxide solution is now added to each tube, and standard vanadium solution is run into the non-vanadium steel solution until the desired coloration is obtained at equal volumes. In the case of steels containing chromium, a quantity of potassium dichromate corresponding with the amount of chromium in the steel must be added to the non-vanadium steel. W. P. S.

Electrolytic Deposition of Antimony. NEWCOMB K. CHANEY (*J. Amer. Chem. Soc.*, 1913, **35**, 1482—1490).—Antimony may be deposited, but not quantitatively, from electrolytes containing ammonium, sodium, and barium lactates; tin is not deposited from these electrolytes.

The conditions for the quantitative deposition of antimony from an ammonium sulphide electrolyte were worked out. It was found that incomplete deposition is due to the fact that antimony is appreciably soluble in colourless ammonium sulphide, and therefore, for complete deposition, it is necessary for the concentration of ammonia and ammonium sulphide to be made negligible towards the end of the electrolysis. This can be effected by electrolysing at boiling temperature, the ammonia and ammonium sulphide being thus expelled or oxidised to ammonium sulphate. The deposits of antimony thus obtained are like polished platinum in appearance. An essential condition for the satisfactory progress of the electrolysis is the proper initial concentration of the ammonium polysulphide. This is best obtained by making two solutions: (*A*) Concentrated aqueous ammonia is saturated with hydrogen sulphide in the presence of powdered sulphur, the excess of which is filtered off after long shaking. (*B*) A concentrated solution of ammonia is saturated with hydrogen sulphide. For the electrolysis, one volume of *A* is mixed with six volumes of *B*, and added drop by drop to

the antimony solution until a clear liquid is obtained. With rotating electrodes 0·24 gram of antimony can be deposited in an hour, using a current density of 1 ampere per sq. dcm. Since tin may be deposited from the same electrolyte, a method of estimating the total tin and antimony is given.

Of the alkaline earth sulphides, that of calcium was found to be best suited for the deposition of antimony. Details of the method are given, but it is somewhat cumbersome, and is liable to give high results. It was found possible to separate tin from antimony by the precipitation of the tin as stannic hydroxide and electro-deposition of the antimony in a solution of calcium sulphide, but further work is necessary before the method can be depended on.

Quantitative results for antimony could not be obtained from ammonium, sodium, and potassium tartrate, or tartaric acid electrolytes. T. S. P.

Volumetric Method for Estimating *o*-, *m*-, and *p*-Cresols, Thymol, and Phenol. L. V. REDMAN, A. J. WEITH, and F. P. BROCK (*J. Ind. Eng. Chem.*, 1913, 5, 831—830).—Rapid and trustworthy estimations of *o*-, *m*-, and *p*-cresol, phenol, and thymol may be made by treating their dilute solution with *N*/30-iodine solution, adding sodium hydrogen carbonate until the mixture is about *N*/2 (compare A., 1911, ii, 546), shaking the mixture for one minute, acidifying the solution, and titrating back the excess of iodine. A series of equations is given for calculatng the quantity of phenol, *m*-cresol, and the sum of the *o*- and *p*-cresols in the presence of each other in any combination or proportion if two quantities are known, namely, the weight of the mixture taken and the amount of iodine absorbed. The error is about 0·2% for each substance present. W. P. S.

Detection of Small Amounts of Dextrose in Urine. SYDNEY W. COLE (*Lancet*, 1913, Reprint, 6 pp.).—The method is based on the reducing power of dextrose after other reducing substances and lactose have been removed by treatment with charcoal. Ten c.c. of the urine are boiled with 1 gram of pure blood-charcoal, then cooled, shaken for about five minutes, and filtered. The filtrate is received in a test-tube containing 0·5 gram of anhydrous sodium carbonate, and, after the addition of six drops of glycerol, the mixture is boiled for fifty seconds. Four drops of a 5% copper sulphate solution are now added, and the mixture is left without further heating for one minute. With normal urine, the solution retains its blue colour, a small amount of phosphates being precipitated. If dextrose is present to the extent of 0·02%, or more, above the average normal amount, the blue colour is discharged, and a yellow precipitate of cuprous hydroxide forms. In the case of urines containing much lactose, the treatment with blood-charcoal must be repeated in order to remove this sugar. Lactose may be detected by heating the urine with blood-charcoal, collecting the latter, and extracting it with hot acetic acid. The acetic acid solution is then used for the preparation of the lactosazone, m. p. 200°. W. P. S.

Method of Estimating Sugar in the Blood. IVAR BANG (*Biochem. Zeitsch.*, 1913, **56**, 159).—A reply to Hatta's criticisms (this vol., ii, 735) on the author's method of sugar estimation. S. B. S.

Quantitative Estimation of Mannitol. JAN SMIT (*Chem. Weekblad*, 1913, **10**, 894—907).—An application of Wagenaar's glycerol estimation process (A., 1911, ii, 663) to the quantitative estimation of mannitol. The experimental details are similar. Ammonium compounds must be eliminated by boiling with alkali; amino-acids by precipitation with phosphotungstic acid, or by transformation into hydroxy-acids by means of nitric acid; sugars by fermentation with an appropriate culture; hydroxy-acids by precipitation as calcium or lead salt; glycerol by extraction with a mixture of alcohol (1 vol.) and ether ($1\frac{1}{2}$ vols.); hexitols, such as sorbitol and dulcitol, by the formation of an acetal derivative with benzaldehyde. The amount of mannitol is not strictly proportional to the cupric hydroxide dissolved, but an empirical table is given showing the proportions of mannitol corresponding with 0·25 to 29·1 c.c. of $N/10$-thiosulphate. It is important to have the concentration of the alkali $4N$, but the temperature has little influence on the results obtained. A. J. W.

Estimation of *d*-Lactic Acid in Body Fluids and Organs JUNJI YOSHIKAWA (*Zeitsch. physiol. Chem.*, 1913, **87**, 382—417).—The relation between the rotatory power and concentration of solutions of lithium lactate is established. Solutions of zinc lactate are warmed with lithium carbonate, filtered, and polarised, when the *d*-lactic acid present is accurately estimated. The presence of *dl*-lactic acid does not disturb the polarisation, neither does lithium acetate have any effect. Normal urine contains no *d*-lactic acid. Added lactic acid can be determined in urine by the polarimetric method, treatment with lead carbonate being unnecessary. The best results are obtained when the lactic acid is extracted with ether from the urine made acid with phosphoric acid. In muscle about 94% of added *d*-lactic acid is indicated by the polarimetric method. *d*-Lactic acid is formed on autolysis of muscle without the intervention of micro-organisms. Similar results were obtained with the liver. E. F. A.

Detection and Identification of Malonic Acid. J. BOUGAULT (*J. Pharm. Chim.*, 1913, [vii], **8**, 289—294).—The formation of cinnamylidenemalonic acid is suggested as a means of identifying malonic acid in a mixture of oxidation products. Particulars are first given of the yields of cinnamylidenemalonic acid obtained when free malonic acid or its sodium or calcium salt is treated with cinnamaldehyde in presence of acetic acid, and it is shown that the inorganic salts and organic acids, likely to occur with malonic acid in mixtures resulting from oxidation experiments, do not seriously interfere with this condensation.

The solution resulting from the oxidation is treated with excess of sodium carbonate, the filtrate, after neutralisation with acetic

acid, evaporated to dryness, and the residue washed with 6... alcohol. The residue left on evaporating this solution is treated with 60° alcohol, and the residue from this solution is mixed with cinnamaldehyde and acetic acid and heated in a closed tube during ten hours. The product is then saturated with sodium carbonate, the solution filtered, and the cinnamylidenemalonic acid isolated by adding hydrochloric acid (compare Riiher, A., 1904, i. 894).

T. A. H.

Estimation of Fixed Organic Acids and a New Method for the Estimation of Citric Acid in Wines and Musts. L. MATHIEU and L. FERRE (*Ann. Chim. anal.*, 1913, **18**, 352—355).—The following procedure is recommended for the estimation of tartaric, malic, and citric acids: (1) Separation of the mixed acids by the process described by Mestrezat (A., 1906, ii, 635), and estimation of the lactic acid by Moeslinger's method. (2) Estimation of the tartaric acid by Kling's method (A., 1912, ii, 1006). (3) Oxidation of the mixture of the three acids by permanganate in both acid and alkaline solution. In acid solution, 1 gram of potassium permanganate oxidises 1·447 grams of tartaric acid, 2·078 grams of malic acid, or 1·820 grams of citric acid, whilst in alkaline solution the same quantity of permanganate oxidises 0·620 gram of tartaric acid, 0·615 gram of malic acid, or 0·380 gram of citric acid.

W. P. S.

A Microchemical Method for the Determination of α- and β-Amino-acids and Certain Derivatives: in Proteolysis, Blood and Urine. PHILIP A. KOBER and KANEMATSU SUGIURA (*J. Amer. Chem. Soc.*, 1913, **35**, 1546—1584. Compare A., 1912, 952, 953).—The method described earlier for the formation of complex copper compounds by the interaction of copper hydroxide and an amino-acid, peptide, or peptone in neutral or slightly alkaline solution has been increased in accuracy by the addition of a suitable solution of sodium borate and boric acid, which prevents the otherwise slightly excessive precipitation of copper.

It is shown that the process can be applied to the accurate and rapid estimation of amino-acids, peptides, and peptones in physiological material.

The copper complexes of amino-*n*-hexoic acid and of phenylglycine are exceedingly sparingly soluble, and, indeed, these acids will precipitate the copper from solutions of all the other complexes examined excepting that of histidine; small quantities of this substance can therefore be readily estimated in mixtures.

D. F. T.

Estimation of Formaldehyde in Fumigators and Commercial Solutions. JACK J. HINMAN (*J. Ind. Eng. Chem.*, 1913, 5, 752—755).—A comparison of various methods which have been proposed for the estimation of formaldehyde and its isomerides showed that the method of Haywood and Smith (A., 1905, ii, 771) and that of Seyewetz and Gibello (A., 1904, ii, 521) are the most

trustworthy. Kleber's method (A., 1904, ii, 371) may also be used, and will be found convenient when a considerable number of estimations have to be made. Legler's ammonia method yields low results (compare A., 1904, ii, 98). W. P. S.

A New Method of Estimation of Urea in Blood. ELI K. MARSHALL, jun. (*J. Biol. Chem.*, 1913, **15**, 487—494).—The method adopted is to convert urea into ammonium carbonate by the urease of soja-bean, and then to estimate the alkalinity. If the ammonia is removed by an air current as in Folin's method, satisfactory results are obtained without a preliminary removal of the proteins. W. D. H.

Estimation of Urea in Urine. ELI K. MARSHALL, jun. (*J. Biol. Chem.*, 1913, **15**, 495—496).—The same method (preceding abstract) may be employed for the urine, and gives better results than the rapid clinical method previously recommended. W. D. H.

Plant Micro-chemistry. Identification of Alkaloids in Sublimates. OTTO TUNMANN (*Pharm. Zentr.-h.*, 1913, **54**, 1065—1068. Compare this vol., ii, 351).—Reactions are given for distinguishing caffeine from theobromine when these alkaloids have been obtained as sublimates. If the sublimate is submitted to the vapours of hydrochloric acid, caffeine yields a crop of crystals within a few minutes, whilst theobromine remains as a white powder. A 10% tartaric acid solution dissolves caffeine readily, but theobromine remains insoluble. Caffeine also dissolves in a concentrated aqueous chloral hydrate solution; theobromine, only when the mixture is heated. These chloral hydrate solutions of the two alkaloids deposit characteristic crystals; in the case of theobromine the crystals appear as spherical masses of needles, whilst caffeine yields hexagonal plates, with needle-shaped crystals developing on the edges of the plates. W. P. S.

The Use of the Folin Method for the Estimation of Creatine and Creatinine. WILLIAM H. THOMPSON, THOMAS A. WALLACE, and HAROLD R. S. CLOTWORTHY (*Biochem. J.*, 1913, **7**, 445—465).—The degree of conversion of creatine into creatinine by boiling with hydrochloric acid is inconstant; it is therefore better to use creatinine picrate for the preparation of the control of the standard dichromate solution. In development of the colour in the Folin method, the optimum time and temperature is seven to twenty-five minutes at 117—120°. The amount of alkali found best is that recommended by Folin.

In urine the darkening of the pigments by acid introduces an error, which in dog's urine may be as high as 10%. Dextrose up to 3%, does not affect the estimation. Phosphoric is not superior to hydrochloric acid in the presence of dextrose. The recovery of creatine from diabetic urine is accompanied by a loss of 5%; this is attributed to the effect of acetoacetic acid. W. D. H.

Precipitation by Zinc Salts of the Purine Bases from Urine and Meat Extracts. ERNST SALKOWSKI (*Biochem. Zeitsch.*, 1913, **55**, 254—259).—The author emphasises the value of his process for separation of the purine substances (this vol., ii, 639) by zinc chloride. The precipitate does not yield the purine substances directly after decomposition of the zinc compounds with hydrogen sulphide. If, however, the zinc salt is first treated with warm nitric acid in the presence of urea, the bases can be precipitated with silver nitrate. The failure to obtain the purine bases directly is due, either to the presence of albumoses, which inhibit the precipitation, or to the fact that the purine substances are in some form of combination, from which they are only set free after treatment with the hot acid. It is shown by the author that the purine bases can also be nearly quantitatively precipitated by zinc salts even without previous removal of phosphates by calcium chloride and ammonia. Purine substances are not carried down as zinc salts in Böhmer's process for separation of albumoses, owing to the large amount of sulphuric acid present. The author replies to certain recent criticisms of his method (compare Thar and Beneslawski, this vol., i, 935). S. B. S.

The Colour Reactions of Triketohydrindene Hydrate (Ninhydrin). W. HALLE, ERNST LOEWENSTEIN and EGON PŘIBRAM (*Biochem. Zeitsch.*, 1913, **55**, 357—369).—A number of substances containing alcohol, aldehyde, or keto-groups, such as glycerol, ethylene glycol, erythrol, glyceraldehyde, acetone, as well as certain sugars, gives the ninhydrin colour reaction, a fact which depends on the existence of a reducing group. The production of the colour is facilitated by the presence of free hydroxyl ions, and in the presence of alkali, dextrose can give the reaction in the dilution 1 : 100,000. The shade of colour produced depends on the strength of the alkali, and the medium of the reaction. Hydrindantin is an intermediate product, and it is an extremely sensitive indicator for hydroxyl ions. The colour produced by amino-acids with ninhydrin differs from that obtained from the above-mentioned substances, in that it is produced in the cold, in the absence of oxygen, and its intensity is not increased on the addition of alkali. Hydrindantin also gives a blue colour with amino-acids. The mechanism of the two classes of reactions is not clearly explained. The colouring matter produced from ninhydrin is in all cases of colloidal character, and it is influenced by the presence of inorganic salts, the cation playing the chief rôle in the changes produced.
S. B. S.

General and Physical Chemistry.

Refraction and Dispersion of Gaseous Nitrogen Peroxide. CLIVE CUTHBERTSON and MAUDE CUTHBERTSON (*Proc. Roy. Soc.*, 1913, *A*, **89**, 361—369).—In order to ascertain the influence of polymerisation on refractivity and dispersive power, the authors have made measurements of the refractive index and dispersion of gaseous nitrogen peroxide at different temperatures and pressures. If the refractivity, reduced to normal temperature and pressure on the assumption that the dissociation equilibrium remains unchanged, is plotted against the corresponding reduced density, it is found that the points fall on a straight line. By extrapolation, this leads to the values 0·000509 and 0·001123 for the refractivity of NO_2 and N_2O_4 respectively. It thus appears that polymerisation increases the refractivity by about 10·5%. In comparison with the refractivities of the constituent elements, that of a molecule of NO_2 is greater by about 21%.

The dispersion measurements show that the dispersive power of a molecule of NO_2 in the red and green is considerably greater than that of a molecule of N_2O_4. H. M. D.

Optical Properties of the Four Carbon-atom Ring. SERGEI V. LEBEDEV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1388—1390. Compare this vol., i, 1285).—The author has measured the refractivities of a number of *cyclo*butane derivatives, including several terpenes. In order to obtain the value of the optical exaltation of the four carbon-atom ring, the exaltation of the unsaturated compound is diminished by 0·51, which Auwers and Ellinger (A., 1912, i, 187) found to be the mean value of the exaltation for the increase caused by the presence of a semicyclic linking; this difference is then divided by the number of rings. With hydrogenised hydrocarbons, the magnitude of the exaltation is divided directly by the number of rings. The values thus obtained are as follows: From the trimeride of *as*-dimethylallene, 0·63; second tetrameride of allene, 0·41; pentameride of allene, 0·47; hexameride of allene, 0·52; 1 : 2-di*iso*propyl*cyclo*butane, 0·40; 1 : 1 : 2-trimethyl-3-*iso*propyl*cyclo*butane, 0·60; 2-*iso*propyl*cyclo*butanone, 0·71; hydrogenised trimeride of allene, 0·62; hydrogenised trimeride of *as*-dimethylallene, 0·75; hydrogenised first tetrameride of allene, 0·75; hydrogenised second tetrameride of allene, 0·67; hydrogenised pentameride of allene, 0·60. The mean of these twelve values is 0·60 (compare Östling, T., 1912, **101**, 457). T. H. P.

Refractive Indices of Certain Liquid Crystals. WALTHER KAUDE (*Physikal. Zeitsch.*, 1913, **14**, 979—981).—Measurements have been made of the refractive indices of cholesteryl chloride and cholesteryl nitrobenzoate in the liquid crystalline condition. Data are recorded for a series of temperatures and for the red

lithium, the yellow sodium, and the green and blue mercury lines. The index of refraction varies with the temperature according to a linear formula. The light which is transmitted by a layer of the liquid-crystalline substances at grazing incidence is found to be polarised. H. M. D.

Refractive Indices of Gelatin Sols and Gels. GEORGE S. WALPOLE (*Kolloid. Zeitsch.*, 1913, **13**, 241—248).—Experiments have been made to ascertain the influence of concentration, temperature, electrolytes, and gel formation on the refractive index of gelatin. At constant temperature, the value of $(n-n')/g$, where n and n' are the refractive indices of the gelatin solution and of water respectively, and g is the number of grams of gelatin per 100 c.c. of solution, is constant and independent of the concentration of the gelatin. It is calculated that the value of $(n-n')/g$ for dry, ash-free, commercial gelatin is 0·001824 at 17·5°. The addition of salts, acids, and bases is without influence on the refractive index of the gelatin, as is shown by observations on solutions containing ammonium chloride, sulphate, and thiocyanate, hydrochloric acid, and sodium hydroxide. The transition from the sol to the gel condition is also unaccompanied by any change in the refractive index of the gelatin when this is measured by means of the quantity $(n-n')/g$. The conclusions drawn by Frei (A., 1910, ii, 365) from a series of similar experiments are adversely criticised. H. M. D.

Refraction and Magnetic Rotation of Compounds with Acetylenic Function. CHARLES MOUREU, PAUL TH. MULLER and J. VARIN (*Compt. rend.*, 1913, **157**, 679—682. Compare Moureu, A., 1906, ii, 1).—A study of the magnetic rotation and refraction of a number of aliphatic and aromatic substances containing an acetylene linking in varying proximity to a substituted negative group. The values for the triple linking have been obtained from the values found and calculated for heptinene and octinene. The results are in accord with those previously obtained by Moureu for the refraction and molecular dispersion (compare *loc. cit.*). The proximity of the triple linking and a negative radicle produce a more or less marked rise in the refraction in the aliphatic series, this being much accentuated in the aromatic series by the proximity of the phenyl group to the acetylene linking. The magnetic rotation is affected qualitatively in the same manner except in the case of acetylene diacetal, $CH(OEt)_2$·C:C·$CH(OEt)_2$. The magnetic rotation is more sensitive than the refraction to the reciprocal influence of the triple linking and the negative or unsaturated groups, this being particularly manifest in the aromatic compounds, where there is a conjugation of the double linking in the phenyl group and the acetylene linking. W. G.

Resonance Spectra of Iodine under High Dispersion. ROBERT W. WOOD (*Phil. Mag.*, 1913, [vi], **26**, 828—846.* Compare A., 1912, ii, 1018).—The resonance spectra of iodine excited by the

* and *Physikal. Zeitsch.*, 1913, **14**, 1189—1200.

green and yellow lines of mercury have been further examined. Improvements in the method of utilising the exciting light have made it possible to photograph the resonance spectra in the fourth order spectrum given by a large plane grating with an exposure of only twenty-four hours. By operating the mercury vapour lamp with different resistances in circuit, it was found possible to vary the width of the exciting line so as to cover a variable number of iodine absorption lines, and the resonance spectra obtained under these conditions have been carefully compared.

In the earlier work it was assumed that each of the bright resonance lines coincided with one or other of the numerous absorption lines, but it is now found that this is not the case. The vapour always emits a line, the wave-length of which is identical with that of the exciting light. This line, termed the resonance radiation line, is accompanied by companion lines which form a group very similar in appearance to the other groups which appear at intervals along the spectrum. The width of this group of lines is about thirty times the width of the group of absorption lines, which are covered by the mercury exciting line. This indicates that each one of the absorption lines must be responsible for more than one line in each resonance group. From the fact that the characteristic resonance group forms a cluster round the exciting line, and that the widths of the different groups are sensibly the same, it appears probable that each absorption line gives rise to a series of equidistant lines, which are superposed and form the cores of the different groups. These lines are accompanied by companion lines, the position of which depends on the absorption lines which are excited, but for any given absorption line, the position of the companion line and its distance from the core remains constant. By reducing the density of the iodine vapour in the resonance tube, it is found that the band spectrum is emitted. This spectrum is more strongly absorbed by the iodine vapour than the lines of the resonance groups.

There is apparently no phosphorescent effect in the emission of the resonance spectrum. H. M. D.

The Arc and Spark Spectrum of Aluminium in International Normals. RAINER GRÜNTER (*Zeitsch. wiss. Photochem.*, 1913, **13**, 1—19).—Wave-length measurements have been made in the arc and spark spectra of aluminium. The recorded observations, which extend from $\lambda=2100$ to $\lambda=6700$, are expressed in terms of the international normal lines, and compared with the data obtained by Kayser and Runge and by Exner and Haschek. In addition to the line spectrum, aluminium gives a characteristic band spectrum, in which the bands are shaded off towards the red end of the spectrum. H. M. D.

Measurements in the Ultra-violet Spark Spectrum of Metals According to the International System. JOSEF M. EDER (*Zeitsch. wiss. Photochem.*, 1913, **13**, 20—40).—Accurate wave-length measurements have been made of the lines in the ultra-violet spark

spectra of silver, aluminium, arsenic, gold, barium, bismuth, carbon, calcium, cadmium, copper, lead, antimony, tin, strontium, thallium, and zinc between λ 1900 and λ 2400. It is estimated that the wave-lengths of the sharp lines are accurate to 0·01 Å., whilst the weaker lines are probably correct to 0·02 Å.

The wave-lengths of the sharper lines in the ultra-violet spectrum of copper were determined in the first instance in terms of the international scale and by the use of copper alloys as electrodes; the spectra of the other elements were referred to the copper standards. In some cases the spark discharge was allowed to take place between a copper electrode and an electrode of the metal under investigation.

It is claimed that the measurements afford more accurate wave-length data than have hitherto been available for the region examined, and that the accuracy with which dispersion formulæ for quartz prisms may be determined has been considerably increased.

H. M. D.

New Measurements of the Arc Spectra below λ = 3200 for Several Metals. Wilhelm Huppers (*Zeitsch. wiss. Photochem.*, 1913, **13**, 46—88).—The arc spectra below λ = 3200 of the metals zinc, lead, calcium, thallium, cadmium, magnesium, aluminium, copper, silver, and lithium have been measured by means of a quartz spectrograph. The Hartmann formula was used to calculate the wave-lengths of the various lines, and values are obtained of an accuracy of ±0·01 Å. The stronger spark lines, particularly in the cases of silver and copper, make their appearance in the ultra-violet spectrum. A large number of hitherto unmeasured lines are recorded, the more particularly in the case of cadmium. Many of these new lines can be placed in the various series, or can be classified as combination lines. The thallium spectrum is remarkable for the unsharp nature of the lines and the partition of their intensities. The reversals of the lines λ 2379 and λ 2767 are observed in the photographs, but other reversals are not visible in the photographs. Reproductions of portions of the cadmium and thallium spectra are appended to the paper. J. F. S.

Investigations in the Extreme Ultra-violet. Karl Wolff (*Ann. Physik.* 1913, [iv], **42**, 825—839).—A new form of quartz arc lamp is described, by means of which the author has investigated the arc spectra of zinc, cadmium, and mercury in the extreme ultra-violet region, the observations extending up to the limit fixed by the transparency of fluorite. The series lines anticipated by Paschen (A., 1911, ii, 133) have been actually observed, and from comparative observations on the hydrogen spectrum in the Schumann region, it has been possible to assign wave-lengths to several hydrogen lines with an accuracy of the order of one Ångström. These lines and the new lines belonging to zinc, cadmium, and mercury may be utilised as normal lines in the investigation of this region of the spectrum.

Certain lines belonging to carbon and silicon have also been

measured, and Lyman's observation that the helium spectrum contains no lines between $\lambda = 1850$ and $\lambda = 1402$ is confirmed.
H. M. D.

Investigations in the Extreme Ultra-violet.] FRIEDRICH PASCHEN (*Ann. Physik*, 1913, [iv], **42**, 840—842).—The nature of the ultra-violet series of lines found by Wolff (preceding paper) in the spectra of zinc, cadmium, and mercury is discussed with reference to the author's formulæ for principal and combination series of lines.
H. M. D.

Influence of Self-induction on the Spark Spectra of Certain Non-metallic Elements. GENEVIEVE V. MORROW (*Sci. Proc. Roy. Dubl. Soc.*, 1913, **13**, 607—620).—The spectra obtained by sparking gold and carbon electrodes, with and without self-induction, have been examined in an atmosphere of nitrogen, oxygen, hydrogen, chlorine, bromine, iodine, sulphur, phosphorus, boron trichloride, silicon tetrachloride, sulphur dioxide, hydrogen sulphide, carbon dioxide, carbon monoxide, and hydrogen chloride.

It is found that the principal lines of the line spectra of the elements present in the gaseous atmosphere are obtained, and, as a general rule, the intensity of the lines is greatest when self-induction is not introduced. In the case of compounds, only the line spectra of the component elements are observed, the band spectra of the compounds not being seen except in the case of cyanogen. With hydrogen, which was the only electropositive gas examined, the effect of self-induction is to intensify and sharpen the hydrogen lines, and to remove, more or less completely, the lines of gold and carbon. On the other hand, with electronegative gases, such as oxygen and nitrogen, self-induction removes the gas lines and leaves the gold or carbon spectrum more or less unchanged. With chlorine, bromine, and iodine, the effects of self-induction are not so pronounced.

When carbon electrodes are employed, the three bands attributed to cyanogen are seen in almost any atmosphere except hydrogen if self-induction is introduced into the circuit. Without self-induction, only the one band at λ 3883·6 is observed, and this is also found in any atmosphere except hydrogen. H. M. D.

New Burner for Spectroscopic Use. ERNST H. RIESENFELD (*Chem. Zeit.*, 1913, **37**, 1372).—The relative advantages of burners in which a spray of the solution to be investigated is carried by the air into the interior of a Bunsen flame (such spray being obtained by the chemical [Beckmann, A., 1907, ii, 209] or electrolytic [Riesenfeld and Wohlers, A., 1906, ii, 593] evolution of gas in the solution) are discussed. Preference is given to the latter method, for which a greater constancy in the intensity of illumination as well as a greater range in the latter are claimed.

A new burner is described in which the solution to be investigated (about 1 c.c.) is placed in a small glass cup inside the tube of a Bunsen burner, the upper portion of which is preferably made

of glass. About 1 c.c. of nitric acid (10 per cent.) is added, and a particle of granulated zinc. For a sodium flame, it is advisable to use sodium nitrate solution (20%). Fracture of the burner owing to heat is unlikely, provided the flame is prevented from striking back. The flame is not coloured by the constituents of the glass, and, when the cup is not charged, shows only the Swan spectrum and the sodium lines.

H. W.

Influence of Neutral Gases on the Absorption of Sodium Vapour. (A Correction.) KARL FREDENHAGEN (*Physikal. Zeitsch.*, 1913, **14**, 1047—1049. Compare A., 1911, ii, 571; A., 1912, ii, 517).—The very considerable variations in the absorption and dispersion of sodium vapour, which are observed when the pressure in the tube containing the vapour is changed, have been previously attributed to the influence of traces of foreign gases on the sodium vapour. Experiments are now described in which sodium was heated in highly exhausted tubes on the one hand, and in tubes containing helium on the other. Some of these tubes were heated as uniformly as possible, at about 400°, whilst others were only partly immersed in the heating jacket, and the absorption in the different tubes was compared. The observations indicate clearly that the presence of the helium is without influence on the absorption of the sodium vapour, and that the above-mentioned changes in the optical properties are to be attributed to changes in the density resulting from the pressure variations. H. M. D.

A Quantitative Study of Absorption Spectra by means of the Radiomicrometer. J. SAM GUY and HARRY C. JONES (*Amer. Chem. J.*, 1913, **50**, 257—308. Compare A., 1909, ii, 197, 359, 775; 1910, ii, 87, 172, 246; 1911, ii, 166; 1912, ii, 216, 507, 711; this vol., ii, 362).—The authors have studied the absorption spectra of salts of neodymium, praseodymium, nickel, and cobalt over the range λ 6800 to λ 10,000, and at several concentrations by means of a radiomicrometer specially constructed by them. The results are plotted as transmission curves; it is shown that in general the more concentrated the solutions the less the transparency and the broader the absorption bands, but in the more dilute solutions the intensity of the bands was greater, and there is a shifting of the middle of the bands toward the region of greater wave-length on dilution. In the case of salts of neodymium, three bands are observed with their centres at λ 7300, λ 7950, and λ 8700, and two other bands at λ 7150 and λ 9000, which are probably due to the solvent. The reason for increase in the intensity of the bands on dilution is explained on a theory of resonance. It is noticed in many cases that the aqueous solutions of hydrated salts are often more transparent than pure water. This point is carefully studied, and it is shown that the absorption of light by solutions of non-hydrated salts is the same as that of the water contained in the solution, providing that the salt itself has no specific absorption, but in the case of highly hydrated salts the

absorption of the solution is less than that of the pure water. It is thus shown that free water and combined water have different absorptive effects on infra-red rays. The maximum transmission of neodymium salt solutions lies at λ 7600 and λ 8400. Solutions of praseodymium salts are transparent in the infra-red as far as 1·5μ; there are two groups of bands, one in the green near λ 4600, and another near λ 5900. Solutions of nickel chloride show an increasing absorption from λ 5200 to λ 6300, where it becomes complete; from here there is complete absorption to λ 7200, and then the transmission steadily increases to λ 9000 and then decreases to zero at λ 10,000. The absorption of nickel nitrate solutions resembles that of the chloride, but in the case of the sulphate there is no region of complete absorption. The maxima of transmission lie at λ 5400 and λ 9000, and the minima at λ 6900 and λ 11,000. Salts of cobalt have strong ultra-violet absorption, and there is a band in the orange near λ 5000 with increasing transmission toward the red. The infra-red absorption curves of cobalt chloride, nitrate, bromide, sulphate, and acetate have maxima of transmission at λ 5950, λ 7800, λ 9100, and λ 10,600. The transmission curves of all the salts of cobalt studied rise rapidly from λ 5000 to λ 5900; they show a broad, slight absorption over the region near λ 6500, and reach a maximum transmission from λ 7000 to λ 8000. There is a series of small absorption regions near λ 8400, λ 9000, and λ 9800. Beyond λ 10,900 the absorption increases rapidly to the region where water is practically opaque. Beer's law is shown to hold for the infra-red absorption of solutions of neodymium chloride and praseodymium chloride. J. F. S.

Spectro-chemistry of the Cobalt Complexes. YUOI SHIBATA and GEORGES URBAIN (*Compt. rend.*, 1913, **157**, 593—595).—A study of the absorption spectra of solutions ($N/100$ and $N/1000$) of twenty-four complex cobalt salts in the visible and ultra-violet portions of the spectrum, the results pointing towards certain relations between the constitutions of the complex salts and their absorption. Curves obtained by plotting the thickness of the solutions against the frequency limits of absorption show two marked minima in the neighbourhoods of λ 2000 and 3000. These two bands seem to be characteristic of the tervalent cobalt atom, functioning as chromophore. In general, with the exception of the group NO_2, the negative radicles provoke a displacement of the less refrangible band towards the red. The effect of the relative changes in intensity of the two bands is almost always more marked than the displacement effect in the frequency scale. W. G.

Ultra-violet Absorption of Pure Acetone above λ 332 μμ. HANS T. CLARKE and ALFRED W. STEWART (*Physikal. Zeitsch.*, 1913, **14**, 1049—1050. Compare Gelbke, A., 1912, ii, 713).—The absorption of ultra-violet light by pure acetone has been investigated by experiments with layers of thickness ranging from 50 to 400 mm. The curve which is obtained when the wave-length of the limiting transmitted light is plotted against the thickness of the absorbing

layer exhibits no minimum above $\lambda\, 332\mu\mu$, although there is a change in the slope of the curve at $\lambda\, 336 \cdot 5\mu\mu$.

In a note added by JOHANNES STARK it is claimed that this affords clear evidence of the long-waved ultra-violet band, the existence of which he has previously anticipated. H. M. D.

Fluorescence of the Elements of the Sixth Group of the Periodic System. F. DIESTELMEIER (*Physikal. Zeitsch.*, 1913, **14**, 1000).—A claim of priority against Steubing (this vol., ii, 816), in reference to the fluorescence spectrum of sulphur and selenium. H. M. D.

Some Decompositions in Ultra-violet Light. ANTON KAILAN (*Monatsh.*, 1913, **34**, 1209—1244).—The action of a quartz-mercury lamp at a distance of 8 cm. on $N/2$- to $2N$-solutions of acetic, oxalic, malonic, succinic, malic, and tartaric acids in quartz vessels, produced in all cases decomposition, as shown by diminution of the titre with alkali. Acetic acid was decomposed to the greatest extent, and oxalic acid to the least. The presence of the hydroxyl group in the molecule increased the rate of decomposition. The decomposition in N-acetic acid solution amounted to 3·5% after three hours' exposure. No effect was observed in transparent glass vessels. The reaction velocity increases with the time of exposure and with the concentration, although less rapidly than in proportion to the latter, the departure from proportionality being smaller than is the case in the decomposition of iodides and the oxidation of aldehyde. Dissolved oxygen produces little, if any, effect.

No effect was produced on the rotation of fermentation amyl alcohol. In neutral $N/10$-solution, potassium and sodium iodides are less decomposed than the iodides of barium and strontium, but in $N/160$-hydrochloric acid, these iodides and that of magnesium are decomposed to the same extent. The acid increases the rate of decomposition up to $N/800$, but after that only produces a slight effect. Dissolved oxygen is responsible for the liberation of the iodine. In a vacuum, the decomposition may be reduced to less than one-half. The presence of thiosulphate and rise of temperature are without effect, and the liberation of iodine through the formation of hydrogen peroxide plays no important part. Potassium fluoride is not decomposed under these conditions. F. S.

The Physical Chemistry of Photographic Development. C. E. KENNETH MEES (*J. Amer. Chem. Soc.*, 1913, **35**, 1727—1732).—A paper read at the Rochester meeting of the American Chemical Society, 1913. It consists of a review of the physical chemistry of photographic development. T. S. P.

Physico-chemical Studies on Photographic Developers. III. NIKOLAI SCHILOV and EUG. TIMTSCHENKO (*Zeitsch. Elektrochem.*, 1913, **19**, 816—819. Compare A., 1912, i, 966; this vol., ii, 371; also Pinnow, this vol., ii, 398).—In the previous papers it is shown that sodium sulphite plays a definite rôle in the oxidation of quinol.

that it first functions as an acceptor for the peroxide oxygen, and later forms complex additive compounds with the quinol, which are oxidised regularly and slowly without the formation of tarry matter. In the present paper the sulphite is replaced by other reducing agents. Sodium arsenite is first investigated, and it is shown that it acts mainly as an acceptor for the oxygen and uses up about one-half of the oxygen, but probably forms no complex compounds with the quinol. Experiments were made also with hydroxylamine and with hydrazine. Both these substances regulate the oxidation of the quinol in exactly the same way as sodium sulphite, inasmuch as they form a series of complex additive compounds. It is shown that a photographic plate can be developed by quinol in the presence of hydroxylamine. J. F. S.

Oxidation and Preservation of [Sodium] Sulphite–Quinol Solutions. JOHANNES PINNOW (*Zeitsch. wiss. Photochem.*, 1913, **13**, 41—45. Compare this vol., ii, 398).—It is shown that the sodium salt of quinolmonosulphonic acid is the chief product of the first oxidation of sodium sulphite–quinol solutions. This salt has been isolated, and is described as crystallising in small, thin leaflets from methyl alcohol solution. It is also shown that by the addition of 0·05 mol. acetic acid per litre the ordinary quinol–sulphite developer can be preserved for four times the ordinary length of time. In using the acidified developer it is necessary to add twice as much soda solution as is required to neutralise the acid which has been added. J. F. S.

Luminescence. EARL F. FARNAU (*J. Physical Chem.*, 1913, 17, 637—656).—The luminescence produced by a number of substances under a series of conditions have been determined by the author. The experiments include observations on the cathodoluminescence, canal ray luminescence, ultra-violet luminescence, luminescence by heating, luminescence by trituration, chemiluminescence, and crystallo-luminescence of a series of the haloids of sodium, potassium, cadmium, zinc, mercury, lithium, rubidium, and cæsium, together with, in a few cases, the carbonates and sulphates. The author draws the conclusion that luminescence of all kinds is due to a chemical reaction. Increase in the rate of the reaction, brought about either by a catalytic agent or by increase in the temperature, increases the luminescence. The nature of the luminescence is but slightly altered by the nature of the catalyst or the temperature change. The nature of the luminescence in most cases depends only on the metal of the salts, but in a few cases the acid radicle has an influence. The nature of the luminescence is the same no matter how it is produced. J. F. S.

Absorption Measurement of β-Rays. HERMANN STARKE (*Physikal. Zeitsch.*, 1913, **14**, 1037—1038).—Position of the absorption screen with reference to the radioactive preparation and the measuring instrument affects measurements of β-rays, and it is recommended that the screen be placed directly against the ionisation chamber. F. S.

The Excitation of γ-Rays by β-Rays. HERMANN STARKE (*Physikal. Zeitsch.*, 1913, **14**, 1033—1038).—The secondary γ-rays excited by the β-rays of mesothorium were put in evidence by concentrating the β-radiation on to a reflecting plate by means of a powerful magnet. The mesothorium was placed near one pole, and the reflector near the other pole, a sensitive ionisation chamber being placed so that it was screened from direct radiation by a lead block, but not from the reflected radiation. Excitation of the magnet showed a distinct but small effect, which was estimated to be about one-thousandth part of that due to the primary γ-rays. Only those γ-rays capable of penetrating 3 mm. of aluminium could be looked for by this method. F. S.

Determination of Radium by the γ-Ray Method. VIKTOR F. HESS (*Ber. Deut. physikal. Ges.*, 1913, **15**, 1002—1016; *Physikal. Zeitsch.*, 1913, **14**, 1135—1141).—A modified form of Wulf's γ-ray electrometer is described. Observations made with this instrument and a standard radium preparation placed at a fixed distance from the electrometer chamber show that the ionisation current increases as the source of the rays is gradually moved from the middle of the room into close proximity with one of the surrounding walls. When this distance was reduced to 2 cm., the ionisation was found to increase to the extent of 17%. The increase is due to the secondary γ-rays which are emitted by the adjacent wall. The fact that the same increase in ionisation is observed when the radium preparation is enclosed in a lead capsule, indicates that these secondary γ-rays are produced by the primary γ-rays emitted by the active substance. The importance of this effect in connexion with the standardisation of γ-ray electrometers is referred to.

A new compensation method for the rapid evaluation of radium preparations according to γ-ray method is also described. The arrangement resembled that previously described by Bronson, with the exception that the ionised air resistance is replaced by a liquid resistance prepared by mixing xylene and ethyl alcohol in the ratio of 10 volumes to 1, as recommended by Campbell (*Phil. Mag.* 1912, [vi], **23**, 668). H. M. D.

The Influence of Penetrating Radium-rays upon the Iodides of Alkaline Earth Elements. ANTON KAILAN (*Monatsh.*, 1913, **34**, 1245—1268. Compare A., 1912, ii, 522).—The decomposition of the iodides of magnesium, calcium, strontium, and barium in neutral and in feebly and strongly acid aqueous solutions by the penetrating rays of radium is analogous to that of the alkali-metal iodides. Both in neutral and acid solutions, in absolute alcohol magnesium iodide is decomposed more quickly than in water. No connexion was found between the molecular weight and speed of decomposition. The penetrating rays from preparations containing from 80 to 200 mg. of radium (element) produce only from 1/200 to 1/800th of the effect of a quartz mercury lamp at 8 cm. distance, but in spite of the different orders of magnitude, the general reactions appear to be the same in the two cases. F. S.

The Chemical Action of Penetrating Radium Rays. ANTON KAILAN (*Monatsh.*, 1913, **34**, 1269—1289).—No effect within the error of measurement was produced during 2850 hours by the penetrating rays from 106 mg. radium chloride on the rotation of 500 c.c. of a normal aqueous solution of dextrose at 5° to 10°. Small changes were traced to the influence of the acids formed, which occurs to a greater extent with dextrose than with sucrose. Absolute alcohol is oxidised to aldehyde and acid, and there results in addition a formation of water, for the most part not produced by oxidation, but by decomposition of the alcohol. On succinic and malonic acid solutions the penetrating radium rays produce only an exceedingly slight decompositiou, of the same order, compared with that produced by ultra-violet light, as in the decomposition of iodides. No changes could be established in the electric conductivity and dissociation constants of these acids.

The penetrating rays from 42 mg. of radium chloride, acting for 4000 hours on 5 grams of silver nitrate in $N/4$-solution in the dark, reduced about one-thousandth part to metallic silver.

F. S.

Comparison of the Results of the Electromagnetic and the Spectral Analysis of Canal Rays. JOHANNES STARK (*Physikal. Zeitsch.*, 1913, **14**, 961—965).—A comparison is made of the results which have been obtained by the electromagnetic and spectral methods in their application to the analysis of canal rays. Both methods agree in that they show the existence of hydrogen, helium, carbon, nitrogen, oxygen, chlorine, argon, iodine, and mercury ions carrying a single positive charge; of helium, carbon, nitrogen, oxygen, chlorine, argon, and mercury ions with a double charge; of argon, nitrogen, and mercury ions with three charges; and mercury ions with four charges. On the other hand, the existence of sulphur and iodine ions with two charges, and of oxygen, sulphur, and chlorine ions with three charges, is only revealed by the spectral method of analysis, whilst mercury ions carrying five, six, and seven charges are only shown by the electromagnetic method.

It is pointed out that the experimental conditions obtaining in the spectral method of analysis are, generally speaking, more favourable as regards the formation of ions with multiple charges than the conditions which obtain in the electromagnetic method.

H. M. D.

The Multiple Positive Charge of Chemical Atoms. JOHANNES STARK (*Physikal. Zeitsch.*, 1913, **14**, 965—969. Compare preceding abstract).—A theoretical paper, in which the author discusses the mechanism by which positive ions carrying a multiple charge are produced. It is considered that such ions may either be produced directly as the result of a single collision, or indirectly as the result of a series of collisions in each of which an electron is displaced. Since the energy required for the simultaneous expulsion of several electrons from an atom is much greater than that required for the removal of a single electron, it is probable

that high speed rays are favourable to the formation of multiply charged ions according to the former process. Since the ratio of the number of singly charged ions to neutral atoms is very small, it is further probable that the production of multiply charged ions as the result of a single collision with high speed cathode or canal rays is more frequent than the production by the alternative method.

Since the number of positive charges which an atom can take up is in general greater than the number of valency electrons, it must be assumed that electrons which are more intimately associated with the positive nucleus than the valency electrons, can be expelled under favourable conditions, such as are obtained when a gas is subjected to the influence of canal rays. The energy required for the expulsion of the interior electrons is probably much greater than that which suffices for the liberation of the valency electrons.

H. M. D.

[Canal Ray Spectrum of Hydrogen.] ERNST GEHRCKE and OTTO REICHENHEIM (*Ber. Deut. physikal. Ges.*, 1913, **15**, 1063—1064).—The authors criticise the interpretation of the Doppler effect in the canal rays spectrum of hydrogen given by Stark (this vol., ii, 907), and suggest that the outermost maximum on the displacement curve is due to hydrogen atoms carrying two positive charges. This would fit in with the view that the innermost maximum is due to hydrogen molecules carrying a single charge, and the middle maximum to hydrogen atoms with a single charge. H. M. D.

[Lines in the Canal Ray Spectrum of Argon Corresponding with Ions Carrying One, Two, and Three Charges.] JOHANNES STARK and H. KIRSCHBAUM (*Sitzungsber. K. Akad. München*, 1913, 331—353).—From observations of the Doppler effect in the canal ray spectrum of argon, it is shown that the lines in the red spectrum are due to positively charged atoms carrying a single unit of charge. The lines in the blue spectrum are mainly due to doubly charged atoms, but to a certain extent the blue emission is due to atoms carrying three charges. Low speed cathode rays give rise in general to the carriers of the red spectrum, whilst the production of multiply charged carriers is brought about by high speed rays. The transition from the one type of carrier to the others represents a reversible process, and a condition of equilibrium is set up when the conditions of the discharge are kept constant. H. M. D.

The Energy of the Electron Emission of Strongly Heated Substances. ARTHUR WEHNELT and ERIK LIEBREICH (*Ber. Deut. physikal. Ges.*, 1913, **15**, 1057—1062).—Measurements have been made of the saturation currents which are obtained as a result of the emission of electrons by strongly heated platinum wires covered with a layer of calcium oxide, the observations extending over an interval of twenty-four hours. The saturation current is by no means constant, but rises to a maximum, and this is followed by a gradual fall to a much smaller value. The time required for the

attainment of the maximum current diminishes as the temperature is increased. The final value to which the current falls corresponds with the electron emissive power of pure platinum, indicating that the oxide film gradually disappears. These observations afford an explanation of the fact, established by previous experiments, that the emission of electrons by a platinum electrode coated with a film of oxide is not in agreement with Richardson's formula.

H. M. D.

Cause of the Emission of Electrons by Oxide Cathodes. A. GEHRTS (*Ber. Deut. physikal. Ges.*, 1913, **15**, 1047—1056).—The fact that strongly heated electrodes covered with a thin layer of an alkaline earth metal oxide emit large quantities of electrons has been known for some time, and Fredenhagen (*Physikal. Zeitsch.*, 1912, **13**, 539) has suggested that the oxides are decomposed by the current, and that the emission of electrons is a consequence of the chemical recombination of the oxygen with the alkaline earth metal. In the author's opinion the separation of the oxygen is mainly due to thermal dissociation of the oxide, although there may be a certain amount of oxygen liberated as a result of electrolysis. In other respects the author's theory agrees with that put forward by Fredenhagen.

In the absence of a potential difference the dissociated oxygen recombines quantitatively with the alkaline earth metal, but in an electric field some of the oxygen atoms are converted into ions by combination with electrons, and are thus transported to the anode. The fact that the life of an oxide cathode diminishes as the intensity of the discharge increases is quite in accordance with this hypothesis.

Further evidence in support of it has been obtained in a series of experiments with electrodes of platinum, iridium, tantalum, carbon, and tungsten, each covered with a layer of calcium oxide. After employment as cathodes for some time, the layer of oxide was removed, and the surface of the electrode examined with the aid of a binocular microscope. In the case of platinum and iridium, evidence was obtained of the formation of calcium alloys, whilst tantalum is oxidised to the dioxide and carbon gives rise to carbon monoxide. Tungsten proved to be unsuitable for the experiments, for the oxide film becomes detached as soon as the current is passed between the electrodes. These chemical changes are regarded as distinctly favourable to the author's view of the activity of the oxide-covered electrodes.

H. M. D.

Origin of Thermal Ionisation from Carbon. JOHN N. PRING (*Proc. Roy. Soc.*, 1913, *A*, **89**, 344—360. Compare A., 1912, ii, 115).—Further experiments have been made to ascertain whether electronic emission can be attributed to incandescent carbon, the conditions being modified so as to eliminate more completely the large ionisation effects which were found in the earlier work to be due to chemical action. For this purpose, the purification of the carbon and the exhaustion of the surrounding vessel were carried out more perfectly, and the effect of this on the ionisation

was examined at a series of definite temperatures. Experiments were also made, in which small quantities of highly purified helium, argon, nitrogen, hydrogen, carbon monoxide, and carbon dioxide were admitted into the apparatus at known pressures.

The conclusions drawn from the previous observations (*loc. cit.*) are confirmed by the results obtained in the present work. It is found that the more complete removal of absorbed gases from the carbon leads to a further large reduction in the ionisation. From the observations made after the admission of the different gases, it appears that the ionisation increases with the chemical activity in the order: helium and argon, nitrogen, hydrogen, carbon monoxide, and carbon dioxide. It was found possible to trace the absorption and evolution of gas by the carbon by means of the ionisation currents.

The experiments show that the thermal ionisation of carbon is due to chemical reaction between the carbon and the surrounding gas. If electronic emission occurs at all, the effect must be very small in comparison with that which can be attributed to chemical action. H. M. D.

Photo-electric Emission of Electrons. ROBERT POHL and P. PRINGSHEIM (*Physikal. Zeitsch.*, 1913, **14**, 1112—1114. Compare A., 1912, ii, 317, 618).—From the data for lithium, sodium, potassium, and rubidium, it appears that the wave-length corresponding with the maximum of the selective photo-electric effect is approximately inversely proportional to the radius of the atom. The resonance frequency is, however, not entirely determined by the properties of the atom, for it has been found that the superficial oxidation of a layer of colloidal potassium is accompanied by a shift of the resonance maximum to the extent of $20\mu\mu$. On reduction by hydrogen, the original resonance maximum is observed. Other electronegative gases exert a similar effect in shifting the position of the resonance maximum.

The normal photo-electric effect is also influenced by factors, the nature of which is as yet unknown. From observations on the photo-electric emissive power of a calcium amalgam, it has been found that the emission of electrons commences at about $\lambda\, 365\mu\mu$ in the case of a freshly prepared liquid surface. At the end of an hour, the limiting wave-length has shifted its position about an octave, and is situated in the ultra-red region. H. M. D.

The Photo-electric Effect of Metallic Compounds. B. A. DIMA (*Compt. rend.*, 1913, **157**, 590—593. Compare this vol., ii, 465).—The author has confirmed his previous results that the photo-electrical effect of similar compounds of the same metal diminishes with increase in valency of the metal, by studying the oxides of molybdenum and manganese. It is necessary to use the anhydrous oxides, as their hydrates produce a much feebler emission. From a study of numerous series of oxides he draws the conclusion that the phenomenon of photo-electrical fatigue is only exhibited very slightly by the highest oxides, but to a greater extent by the lower

oxides. In the case of molybdenum trioxide, an increase of 25% was noticed in the emission by prolonging the exposure to ultra-violet light for two hours. At the same time reduction appeared to have taken place at the surfaces exposed to the light. Bromides give a photo-electrical effect intermediate between those of the corresponding chlorides and iodides, and, except in the case of cadmium salts, the effect is increased with increase in the atomic weight of the halogen. W. G.

Connexion Between Ionisation by Collision and Electron Affinity. J. FRANCK and G. HERTZ (*Ber. Deut. physikal. Ges.*, 1913, 15, 929—934; *Physikal. Zeitsch.*, 1913, **14**, 1115—1117).—In order to account for the phenomena of electric discharge through the inert gases, it is necessary to assume that the collisions between the molecules and the electrons are elastic in character. For other gases the elastic nature of the collisions will decrease as the electro-negative character of the gas increases. Observations on the reflexion of electrons by gas molecules indicate that all electrons with speeds smaller than that corresponding with the ionisation potential undergo reflexion in the case of helium. Similar experiments with hydrogen show that only a certain proportion of the electrons are reflected, and in the case of oxygen the reflected electrons are very small in number. These facts indicate that the phenomenon of ionisation by collision is intimately connected with the affinity of the gas molecules for electrons.

In view of the elastic nature of the collisions in the case of the inert gases, the authors draw the conclusion that the influence of an electric field on the electrons present in such a gas is not determined by the length of the free path, but that the accelerating influence of the field is cumulative in its action when the electrons are subjected to a succession of collisions. Ionisation by collision will take place as soon as the potential difference at the electrodes exceeds the ionisation potential. The current potential curves for helium and neon have been examined, and the fact that the curves show a series of breaks at intervals equal to the ionisation potential is quite in accord with the authors' views on the nature of ionisation by collision in the case of these inert gases. H. M. D.

Radium and Radium-emanation in the Water and Deposits of Lake Balaton, Hungary. D. V. LENKEI (*Zeitsch. Kryst. Min.*, 1913, 53, 65; from *Magyar.-balneolog. Értesitö*, 1910, 3, Nos. 5 and 6).—As determined with the electrometer, the water contains 0·0064—0·0224 millionth of a cubic millimetre of emanation per litre; and the mud and sand 0·13—0·85 millionth mg. of radium per kilogram. L. J. S.

Quantitative Estimation of Radium by the Emanation Method. ERICH EBLER (*Zeitsch. angew. Chem.*, 1913, **26**, 658—661).—An apparatus is described for estimating the amount of radium in solutions by the emanation method, consisting essentially of the flask to hold the solution, with capillary leading-in tube and tap,

ground to a small condenser provided at the upper end with a tap, which in turn is ground to one end of a bulb closed by two taps. The solution is boiled in a partial vacuum, and, when the emanation is driven out, saturated salt solution is admitted through the leading-in tube to drive all the emanation into the bulb, which is then detached, and the emanation admitted to the ionisation chamber of an electroscope. The measurement follows the usual method. F. S.

Determination of Valency of Radium by means of Electric Endosmose. HERBERT FREUNDLICH and G. VON ELISSAFOFF (*Physikal. Zeitsch.*, 1913, **14**, 1052—1057. Compare A., 1912, ii, 419).—The electric endosmose method allows the valency of a metal to be determined in excessively small quantity. With a concentration of 50 micromols., the difference between uni-, bi-, and tervalent ions can be determined with from 0·01 to 0·001 mg. Curves, in which the volume of liquid transported is plotted against concentration, show that radium clearly is bivalent, and accords with magnesium and barium, when the behaviour of these ions is compared with that of sodium on the one hand, and chromium, aluminium, and zirconium on the other. No disturbing effects were observed due to the action of the rays on the electric double layer, the behaviour of radium being quite analogous to that of barium. An attempt was made similarly to find the valency of actinium-X, but, although the measurements indicated that it was bivalent, later observation showed that an impurity must have been present. F. S.

Attempts to Separate Radium-*D* from Lead. FRITZ PANETH and GEORG VON HEVESY (*Monatsh.*, 1913, **34**, 1393—1400).—Even although no practical separation of lead from radium-*D* were possible, a slight enrichment of the radioactive constituent would be of great theoretical importance. Numerous attempts have been made in this direction with results completely negative. Earlier observations which apparently gave positive results may be ascribed to the separation of the later products, radium-*E* and -*F*. Among the methods unsuccessfully tried were (1) by precipitation of lead chloride solution at 100° with dilute sodium thiosulphate and with hydrofluoric acid; (2) with quadrivalent lead compounds, by precipitation of a lead chloride solution, saturated with chlorine, with ammonium chloride, whereby ammonium plumbichloride is precipitated; by passing carbon dioxide through a solution saturated with lead chloride and hydrogen chloride (H_2PbCl_6), whereby the lead chloride is fractionally precipitated; and by precipitation of lead dioxide by addition of hydrogen dioxide or bromine water to a solution of lead hydroxide in sodium hydroxide, or of bromine water to lead acetate; (3) by adsorption methods, as by precipitation of barium sulphate or silicofluoride in lead nitrate solution, or barium chloride in a lead chloride solution by saturating with hydrogen chloride; also by separating iron from lead chloride solution by the acetate precipitation, by adding potassium per-

manganate and alcohol to lead chloride solution, and by boiling the latter with flowers of sulphur; (4) by distillation of lead chloride in carbon dioxide at 1000°; (5) by electrolysis in solution, under varying conditions, so that part of the lead separates on the cathode and part on the anode as dioxide, and of molten lead chloride, pure or mixed with potassium chloride; (6) by dialysis of lead nitrate through parchment paper or animal membrane and diffusion of lead chloride solution. The causes of error (presence of radium in the radio-lead, variation in the β-rays of radium-*E* used in the measurements, due to absorption in the material and secondary radiation) are briefly pointed out. F. S.

The Electrochemical Identity (Vertretbarkeit) of Radio-elements. FRITZ PANETH and GEORG VON HEVESY (*Monatsh.*, 1913, **34**, 1593—1603).—The question was examined whether the chemical identity of groups of radio-elements with other elements and among themselves would extend to the electro-chemical behaviour and explain the open questions, such as the frequent activisation of the anode and sharp separation of the *B*-products by an extraordinarily "noble" potential. The electro-chemical behaviour of radium-*E* and thorium-*C* with respect to bismuth, of thorium-*B* with respect to lead and of radium-*A*, -*B*, and -*C* with reference to bismuth, lead, and polonium respectively, supports this extension. The amount of thorium-*C* deposited on a platinum plate, kept $+0{\cdot}6V$ with reference to a *N*-calomel electrode, in *N*/100-nitric acid solution, is greatly reduced by the presence of a few mg. of bismuth. Decomposition voltages for the radio-elements cannot be determined as a function of the current flowing, for the quantity of the radio-ion is insufficient to carry the whole of the current. They were determined by plotting the amount of radio-element deposited during one hour as function of the cathode potential, and in this method a sudden increase in the amount deposited, instead of a sudden increase of current strength, indicates the decomposition voltage. By this means the progress of deposition at potentials higher than the decomposition voltage may be determined. For thorium-*C*, in presence of bismuth, the sudden increase occurs at $-0{\cdot}08V$, an immersed bismuth plate showing the potential $-0{\cdot}082V$. For thorium-*B*, in presence of lead, deposition occurs with perceptible amounts of lead at $-0{\cdot}44V$, but in absence of lead already at $-0{\cdot}33V$. The anodic deposition of thorium-*B* in absence of lead showed a sudden deposition between $1{\cdot}0$ and $1{\cdot}1V$, which is very near to that of lead dioxide. The thorium-*B* is deposited no longer as metal, but as dioxide.

For the radio-elements, electrode potential is of the first importance, the passage of the current, and hence the difference between anode and cathode, is quite a secondary consideration. With three platinum electrodes in a solution of thorium-*B* + -*C*, an anode, a cathode, and a third currentless electrode, and a feeble current strength arranged to give an anode potential the same as that between the third electrode and the solution, there is no difference in the amounts of radioactive matter deposited on the

anode and the third electrode. By gradually increasing the current strength, the potential of the cathode to the solution may be changed from positive to negative, with reference to the calomel electrode, and so a continuous series of potential differences may be obtained. In the anodic metallic deposition of the radio-elements, the anode behaves as a strongly positively polarised cathode, and this explains the anodic deposition of polonium. When the separation of a radio-element from another in a high state of purity is desired, the addition of an appreciable quantity of an element "identical" with the other element is recommended; for example, in separation of pure thorium-C from thorium-$B+C$, lead should be added, the action being analogous to the prevention of adsorption of uranium-X, for example, by presence of thorium.

F. S.

Behaviour of Radio-elements in Precipitation Reactions. KASIMIR FAJANS and PAUL BEER (*Ber.*, 1913, **46**, 3486—3497).—A detailed discussion is given of the evidence that a radio-element in infinitesimal amount is precipitated with a filterable quantity of the precipitate of a common element whenever under the conditions the radio-element itself would be precipitated were it present in precipitable amount. The determination of the chemical nature of a radio-element, not identical in properties with any of the common elements, depends on this behaviour, which, although generally considered obvious, is shown to be difficult to account for. Abnormal adsorption phenomena appear to influence the precipitation less than might be expected.

Although radium-A is precipitated with mercury as sulphide and chromate, it is distinguished from mercury by being precipitated with bismuth in strongly acid solution as phosphate. Radium-A is distinguished from tellurium by the fact that when precipitated with copper and tellurium sulphide, it is not dissolved from the precipitate by ammonium sulphide, but remains undissolved with the copper sulphide. This difference is analogous to that between antimony and bismuth. Were it possible to obtain radium-A (or polonium, with which it is identical) in weighable amounts, it would, unlike tellurium, give a sparingly soluble chromate and phosphate.

The precipitation of radio-elements with other precipitates shows that the solubility product need not be attained before precipitation takes place. The influence of adsorption and the possibility that the radio-elements are present as colloidal solutions (Paneth) require further investigation.

F. S.

Measurement of Radioactive Substances in the Guard-ring Plats Condensor. L. FLAMM (*Physikal. Zeitsch.*, 1913, **14**, 1122—1125).—The mathematical expressions connecting the ionisation with the distance apart of the two plates of a guard-ring plate condensor are developed with special reference to the case where the space is uniformly filled with emanation, with a view to the ultimate construction of a standard form of measuring

apparatus, which will enable absolute measurements of quantities of emanation to be undertaken without the uncertainty attaching to the employment of standard solutions of radium. Tables are supplied for some of the quantities entering into the mathematical expressions. Experiments, with one plate uniformly covered with a layer of polonium, on the variation of the ionisation current with distance between the plates, are shown to agree with the calculated ionisation currents when corrected for a certain small loss of ionisation due to the absorption of the α-rays in the layer of polonium itself. Possibly there is a small effect due to condensed films of moisture. F. S.

The Extraction of Polonium. FRITZ PANETH and GEORG VON HEVESY (*Monatsh.*, 1913, **34**, 1605—1608).—Radio-lead from pitchblende serves as a raw material for the extraction of polonium. The hot saturated solution of the lead nitrate is left to crystallise, the mother liquor is separated by centrifuging, and after being slightly diluted is electrolysed with platinum electrodes and a feeble current, a few mg. of bismuth being added to diminish the separation of radium-*E*. The cathode potential must not exceed $-0.8V$, which corresponds, in the solution described, with 0·16 milliampere per cm.^{2}, but if freedom from radium-*E* is desired, a potential of $-0.5V$ or 0·4 ma. per cm.^{2} may be used. Stirring is advantageous both in electrolysis and also in deposition on copper, which is an equally good method. If polonium free from lead and radium-*D*, but not from radium-*E*, is required, so much concentrated nitric acid is added that lead is no longer cathodically deposited. Under these conditions most of the polonium can still be separated at the cathode. By volatilisation at 1000°, all but 0·1% of the polonium may be removed from the electrodes, which is difficult to do by boiling with acids. The polonium vapour condenses preferably on palladium and platinum, in special degree on the former, rather than on gold, copper, nickel, or the walls of a quartz tube. F. S.

The Solutions of Radioactive Products. TADEUSZ GODLEWSKI (*Le Radium*, 1913, **10**, 250—264).—A platinum plate, coated with the active deposit of actinium (by immersion, negatively charged, in the emanation) was made the anode in purified water, a similar platinum plate being the cathode. A notable proportion of the active deposit was found to have been transported to the cathode. Detailed examination showed that this occurs only when the active plate serving as anode had previously played the part of cathode during electrolysis. When well saturated with hydrogen in this way, and when considerable voltages were employed, two-thirds of the active deposit could be transported to the cathode in purified water.

When purified water, saturated and left some hours with radium emanation, is electrolysed for ninety seconds between platinum electrodes with 220 volts, radium-*A* is deposited on the anode with about one-third of the equilibrium amount of radium-*C*, whilst

on the cathode radium-*B*, with about one-third to one-quarter of the equilibrium amount of radium-*C*, is found. The ratio of radium-*C* on the cathode to that on the anode is usually between one and two. When electrolysis immediately follows saturation with emanation, so that only radium-*A* is present, the latter is still deposited on the anode. In all these experiments in purified water only a fraction of the products present in the liquid is deposited, even after electrolysis has proceeded many hours. The voltage affects the amount deposited, but not the ratio of the anode and cathode activity.

The theory is advanced and supported by numerous experiments that the radioactive matter is present in the colloidal state, and that hydrosols, not ions, are being dealt with, the transport of the products being due to electrophoresis, rather than electrolysis. It was shown that the addition of positive ions, such as hydrion, cause a strong diminution of the anode activity and an enhancement of the cathode activity, whereas negative ions, such as hydroxyl, act oppositely, increasing the anode activity and decreasing the cathode activity. Multivalent ions, such as aluminium and citric acid ion, act much more powerfully than the univalent ions. The ratio of cathode to anode activity can so be varied in the proportion of 40,000 to 1 in the direction predicted from the theory of colloids, and in a manner impossible to account for if the radioactive products existed as ions. Radium-*A* exists as a negative, radium-*B* as a positive hydrosol, whilst radium-*C* exists as both. The effect of a positive ion is to stabilise the positive hydrosol and to neutralise and ultimately reverse the sign of the negative hydrosol. For negative ions the reverse is the case. The results obtained show that the solutions of radioactive products are of the nature of colloidal solutions. F. S.

Radioactivity of Tyrol Mineral Spring. V. MAX BAMBERGER and KARL KRÜSE (*Monatsh.*, 1913, **34**, 1449—1467. Compare this vol., ii, 278).—Further results are given for numerous Tyrolese springs embodied in tables as before. The amount of emanation in the water is given in Mache units, the greatest being for the springs of Villnösstal, where the rock is described as graphite quartzite, and the number of Mache units is from 66 to 90. F. S.

Dielectric Constants of Vapours. G. POHRT (*Ann. Physik*, 1913, [iv], **42**, 569—584).—A Wheatstone bridge method for the measurement of the dielectric constants of gases and vapours is described, in which the null point is determined in two experiments in which two different values are given to the pressure of the gas or vapour in one of the condensors. It is estimated that the mean error of the measurements is only 0·2 to 0·3% of the magnitude $(\epsilon - 1)$, where ϵ is the dielectric constant.

The results obtained for a large number of organic substances are recorded, and, where possible, compared with those given by previous observers. H. M. D.

The Effect of Light on the Electrical Charge of Suspended Particles. STEWART W. YOUNG and L. W. PINGREE (*J. Physical Chem.*, 1913, **17**, 657—674).—The rate of migration of a number of suspensions, under the influence of a potential fall, has been observed by the authors. The suspensions examined have been those of substances charged either negatively or positively, and include arsenic sulphide sols, ferric hydroxide sols, gum mastic, resin, chlorophyll, and bacterial preparations of *Sarcina flava*, *S. rosea*, and *Bacillus prodigiosus*. In all cases the rate of migration is influenced by light; in the case of arsenic sulphide, ferric hydroxide, and the bacteria, the velocity of migration is reduced by illumination, whilst in the other cases mentioned it is increased. The amount of change in some cases reaches 100%. The authors offer two hypotheses to explain the action in the case of the inanimate suspensions: (1) The influence of light is to affect the degree of dispersity of the suspended matter, increasing it in the case of an acceleration, decreasing it in the case of a retardation; (2) the influence of light is to increase the static charge on the particles in the case of acceleration, and to reduce it in the case of retardation. The latter hypothesis alone applies to the bacterial suspensions. J. F. S.

Influence of the Gas and the Electrode Material on Short Spark Discharges Between Metals. E. TAEGE (*Physikal. Zeitsch.*, 1913, **14**, 1041—1042).—The observations described were made with a coupled discharged circuit, in which a spark gap was placed in parallel with a suitable capacity. The distribution of the energy of discharge between the spark gap and capacity circuits was measured, the fraction of the total energy passing through the capacity circuit being regarded as a measure of the "extinction effect" of the spark gap.

From experiments with the spark gap in an atmosphere of air, oxygen, nitrogen, methane, coal-gas, hydrogen, ammonia, and chlorine, it appears that the extinction effect of the spark discharge increases with the thermal conductivity of the gas and with the mobility of the gaseous ions. In presence of the vapours of benzene, carbon tetrachloride, ethyl alcohol, and water, the extinction effect shows a marked increase.

For different electrode materials, the extinction effect increases in the order: magnesium (aluminium, nickel, zinc) (silver, platinum, copper, brass). The metals enclosed in brackets have approximately the same influence on the extinction effect. It seems probable that the differences in question are determined by differences in the electron emissive powers of the metals.

No evidence has been obtained in support of the view that the extinction effect is dependent on chemical action between the metal vapour and the surrounding gas. H. M. D.

Influence of Various Metals on the Thermo-electric Properties of Iron-Carbon Alloys. EUGÈNE L. DUPUY and A. PORTEVIN (*Compt. rend.*, 1913, **157**, 776—779. Compare this vol., ii. 16).—A study of the modifications produced in the thermo-

electric properties of iron-carbon alloys by the addition of varying amounts of metals commonly employed for preparing special steels, namely, manganese, silicon, aluminium, chromium, tungsten, and molybdenum. Some sixty alloys were examined, divided into two groups, one containing 0·15% carbon, and the other 0·8% carbon, examinations being made in each case of annealed and tempered alloys. The curves obtained by plotting the thermoelectric powers against the amount of metal added show that the metals experimented with divide themselves into two groups: (1) Manganese, silicon, and aluminium give a continuous curve, indicating that these metals, within the limits studied, form solid solutions; (2) chromium, tungsten, and molybdenum give curves which indicate formation of solid solutions, the saturation points of which are given by changes in the directions of the curves, and the formation of carbides. W. G.

A New Hydrogen Electrode and its Applicability. ERNST WILKE (*Zeitsch. Elektrochem.*, 1913, **19**, 857—858).—The electrode described consists of a thin palladium capillary tube sealed at its lower end, and into which hydrogen at constant pressure is pumped. Using this electrode, the potential due to hydrogen ions is set up at once, and constant and reproducible results are obtained. It is shown that after some time the electrode ceases to work rapidly, but that it may be brought to its former sensitiveness by heating it in oxygen. It is also shown that when the electrode is in its most sensitive condition the potential values are not dependent on the nature of the surrounding gas. J. F. S.

Distribution of Solvent Between Solutes. I. Electrical Conductivity and Refractive Index of Mixtures of Aqueous Solutions of Salts of the Alkali Metals. ANTONY G. DOROSCHEVSKI and S. V. DVORSHANTSCHIK (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 1174—1209).—Determinations of the electrical conductivities at 18° of mixtures of aqueous solutions of (1) chlorides, (2) nitrates, (3) carbonates, and (4) sulphates of potassium and sodium, give results which are in agreement with the assumption that solutions of these salts of equivalent concentration are isohydric. Barmwater's formula for the conductivity of mixtures of electrolytes (A., 1899, ii, 274, 396) may be deduced, as a particular case of a general formula, from the law of isohydry, and is applicable to those mixtures which are in agreement with his dilution formula. The latter is valid for the chlorides and nitrates of the alkali metals, but does not hold exactly with the sulphates or carbonates of these metals. The results obtained by the authors for sodium and potassium carbonates and sulphates within the limits of dilution, $v = 10$—100, are found to agree closely with the empirical formula, $\lambda = A - a/\sqrt[8]{v}$, where A and a have the respective values: 179·45 and 114·15 for potassium carbonate, 165·69 and 123·92 for sodium carbonate, 111·265 and 178·37 for potassium sulphate, and 98·10 and 151·90 for sodium sulphate.

In general it is not possible to establish experimentally the exact

conditions of isohydry, the corresponding dilutions being expressible only as lying between limiting values. Consideration of the possible conditions of isohydry renders it highly probable that, in solutions of salts of the alkali metals, perfectly stable systems are formed, in which each molecule of salt is surrnunded by a constant quantity of water.

The refractive index nf a dilute solution of a potassium salt is identical with that nf a solution of equivalent concentration of the sodium salt having the same anion. T. H. P.

A Scheme for the Dissociation of Ternary Electrolytes. CARL DRUCKER, R. GIFFORD, L. GOMEZ, J. GUZMAN, and D. KASANSKY (*Zeitsch. Elektrochem.*, 1913, **19**, 797—808).—Solutions of barium chloride, barium bromide, and zinc chloride have been examined with respect to their innisations. Measurements of the equivalent conductivity, molecular depression of the freezing point, *E.M.F.*, and transport numbers of the ions have been made. If the salts are represented by AB_2, it is shown that the solutions contain the ions $A^{\cdot\cdot}$, $AB^{\cdot}$, AB'_3, B', and undissociated AB_2, and if C_1, C_2, C_3, C_4, and C_5 respectively represent the concentrations of these substances, and C is the total concentration of the salt, the following concentrations were obtained: for $0{\cdot}1N$, $ZnCl_2$, $C_1=0{\cdot}072$, $C_2=0{\cdot}004$, $C_3=0{\cdot}018$, $C_4=0{\cdot}130$, and $C_5=0{\cdot}006$; for $0{\cdot}1n BaCl_2$, $C_1=0{\cdot}070$, $C_2=0{\cdot}015$, $C_3=0{\cdot}015$, $C_4=0{\cdot}140$, and $C_5=0{\cdot}000$. It is shown in all cases that at concentrations above $0{\cdot}02n$ the transport number of the anion increases, which points to the presence of ions of the type AB'_3; below this concentration the value of the anion transport number passes through a minimum, which points to the presence of the ions AB'. J. F. S.

Electrical Conductivity of Mixtures of Two Electrolytes. A. VOJTASCHEVSKI (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1429—1450). —The author has applied to various solutions, each containing two electrolytes, the method devised by Miolati and Pizzighelli (A., 1908, ii, 595) for determining tho composition of complex compounds formed on mixing solutions of two substances.

With mixtures of magnesium and potassium chlorides, the electrical conductivities were measured at 18° for four series of solutions, the concentration of magnesium chloride being constant for each series, whilst the number (x) of gram-mols. of potassium salt per 1 gram-mol. of magnesium salt varied from 0·5 to 10. The four curves showing the relation nf the specific conductivity to x are continuous, and show no break at any point. Similar continuous curves are given by mixtures of magnesium and ammonium chlorides (at 10°, 25°, and 35°), nf magnesium and potassium chlorides, of magnesium chloride and hydrochloric acid, of magnesium and potassium brnmides, nf aluminium and potassium sulphates, of cadmium and potassium iodides, and of cobalt chloride and calcium bromide (compare Jnnes and Uhler, A., 1907, ii, 147, 211).

These results, which indicate the inapplicability of Miolati and

Pizzighelli's method, are not in accord with those obtained by Costăchescu and Apostoi (A., 1912, ii, 528). These authors employed in their experiments cells unsuitable for the measurement of the conductivities of concentrated solutions, and in some cases, for instance, with mixtures of magnesium and sodium sulphates, constructed curves showing breaks from points which really lie on continuous curves.

On the basis of the law of mass action, the author demonstrates that, in general, no break occurs in the magnitude of any property of a mixture of two compounds in solution. The sole exception to this rule is found in the case when the equilibrium constant of the reaction between the two compounds is so large that it may be regarded as infinitely great, and the reaction hence proceeds virtually to completion. Thus, a break in the conductivity curve would be observed when an acid is neutralised by a base, and, in all probability, when ferrous and potassium cyanides react.

T. H. P.

Electrical Conductivity and Diagrams of State of Systems formed by Benzoic Acid with Aniline or Toluidines. A. Baskov (*J. Russ Phys. Chem. Soc.*, 1913, **45**, 1604—1634. Compare Konovalov, A., 1894, ii, 5; Patten, A., 1903, ii, 57).—Investigation of the melting-point curves of the three systems formed by benzoic acid with aniline and *o*- and *p*-toluidines shows the existence in each case of a compound formed of one molecule of the acid with one of the amine. The absence from the melting-point curves of maxima corresponding with these compounds, together with the existence of definite transformation temperatures, indicate that, in the fused condition, each of the three compounds is partly dissociated into its components.

The electrical conductivities of the three systems were investigated at 75°, 100°, and 125°. With those containing aniline or *o*-toluidine, the maximal conductivity corresponds closely with the composition of the definite compound. In the case of the system, benzoic acid–*p*-toluidine, the maximum value of the conductivity is displaced to a marked extent in the direction of excess of benzoic acid; the conclusion is drawn that the compound formed from benzoic acid and *p*-toluidine tends to unite with excess of the acid to give a complex of good conducting properties. In all three systems the temperature-coefficient of conductivity is negative, the specific resistance increasing with rise of temperature; further, the maximal values of this coefficient and of the conductivity are in correspondence. The negative character of the coefficient affords an explanation of the partial dissociation of the definite compound or complex, which conducts well, into its constituents, which show diminished conductivity, such dissociation gradually extending as the temperature is raised.

T. H. P.

High Tension Electrolysis. A Method of Measuring High Voltage Currents. William W. Strong (*Amer. Chem. J.*, 1913, **50**, 213—218).—Very little quantitative work has been

recorded on the phenomena of electrolysis when high voltages are employed, this being largely due to the lack of sources of currents of high and constant potential.

Apparatus is now described which consists of a transformer, and a graduated vessel containing platinum electrodes and an electrolyte, the latter being connected in series with the transformer and corona wire. By suitable means the corona current can be made either positive or negative.

The gases are not evolved at the electrodes in the volume-ratio $2H_2 : O_2$, but it was found that in some cases all the gas moved in the same direction as the electric current. The total quantity of gas evolved was in accordance with Faraday's laws. E. G.

Electrochemical Resonance. VLADIMIR A. PLOTNIKOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1529—1535).—The results of the author's previous investigations have led him to the conclusion that electrolytic conductivity is conditioned, not by any separate property of the solvent, but by a peculiar electrochemical correspondence between the solute and solvent, such correspondence being possibly determined by the relation of the dielectric constant of the solute to that of the solvent.

It is quite probable that in liquids the molecules or groups of atoms exhibit at a given temperature vibrations with a definite periodicity, an appreciable amount of energy being possessed by only some of these vibrations characterised by the internal constitution of the molecules under the given conditions. The existence of such vibrations is supported by the results of spectroscopic investigations (compare Coblentz, *Jahrb. Radioakt. Elektron.*, 1907, **4**, 62). As regards the character of such ionic vibrations, Drude (*Ann. Physik*, 1904, [iv], **14**, 677) showed that they should correspond with the infra-red part of the spectrum, and the most recent investigations on infra-red absorption spectra render it evident that many substances, transparent to ordinary light, exhibit characteristic absorption bands in the region of long waves.

If the period of one of the vibrations characterising the molecule of the solvent coincides with the period of vibration of the ion, the phenomenon of resonance appears. Under the influence of the vibrations of the neighbouring molecules of the solvent the ions acquire sufficient kinetic energy to overcome the forces maintaining the ions in one and the same molecule.

These considerations are extended to the discussion of complex ions. With the difference between the dissociation caused by the resonance of simple ions and of complex ions corresponds a difference in the behaviour of the molecular conductivity on dilution. In the former case the conductivity increases continuously with dilution, the curve being "normal"; but in the latter case, the complex ions break down on dilution, so that the molecular conductivity diminishes and an "abnormal" curve is obtained.

The most favourable condition for resonance is coincidence of the numbers of vibrations of the solvent and the ion, but a feebler resonance may arise with other relations between the numbers of

vibrations, so that a given solution may exhibit simultaneously two different types of conductivity.

The results of Rubens and Hollnagel (A., 1910, ii, 172) and of Nernst and Lindemann (this vol., ii, 103) are quoted in support of the conclusions drawn from the hypothesis of electrochemical correspondence. T. H. P.

Effect of Light on Decomposition Voltages. ALAN LEIGHTON (*J. Physical Chem.*, 1913, **17**, 695—702).—A rubber-coated quartz mercury lamp was immersed midway between the electrodes in an electrolysis cell containing copper sulphate solution. The electrodes were either of carbon or platinum. The decomposition voltage was measured directly when either one or both electrodes were illuminated or when both were not illuminated. It is shown that the decomposition voltage is not affected when the anode alone is illuminated in the case of platinum electrodes, but it is increased when the cathode is illuminated. It is possible to so regulate the voltage that copper can be deposited on the shaded portion of the cathode, but not on the illuminated portion. Graphite is shown to absorb a cuprous salt from the electrolyte, which acts as an anodic depolariser. This reaction is accelerated by light. Using a graphite anode and a platinum cathode, the decomposition voltage can be reduced to 0·4 volt by illuminating the anode. J. F. S.

Magneto-chemical Investigations. Measurement of the Absolute Susceptibility of Water. W. J. DE HAAS and PAUL DRAPIER (*Ann. Physik*, 1913, [iv], **42**, 673—684).—The authors have measured the magnetic susceptibility of water by a hydrostatic null-method, which is described in detail. The value obtained is $\chi = -0{\cdot}747 \times 10^{-6}$ in air at 21°, whilst in hydrogen at the same temperature $\chi = -0{\cdot}721 \times 10^{-6}$ represents the mean result. These values are in good agreement with recent measurements of the specific susceptibility made by other observers. H. M. D.

Measurements in the Electro-magnetic Spectrum of Water with Feebly Damped Vibrations of 65 to 20 cm. Wave-length. H. RUKOP (*Ann. Physik*, 1913, [iv], **42**, 489—532).—A form of apparatus is described, by means of which it is possible to obtain electromagnetic waves of short wave-length covering a range of two octaves. The vibrations are approximately monochromatic and damped to a very small extent. By the aid of this apparatus it has been found possible to determine the electric index of refraction of water with an accuracy of about 0·15%.

The water spectrum shows a number of anomalous dispersion bands in the region submitted to examination, but the complicated dispersion phenomena described by Colley (*Physikal. Zeitsch.*, 1909, **10**, 329, 471) are not confirmed by the author's observations. H. M. D.

The Magneto-optical Kerr Effect in Ferro-magnetic Compounds. IV. PIERRE MARTIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 318—331. Compare A., 1912, ii, 1039).—The Kerr effect

has been investigated in a further series of ferro-magnetic substances with special reference to the form of the dispersion curve. The substances submitted to examination were manganese arsenide (MnAs), manganese antimonide (MnSb), iron carbide, ferrosilicon (containing 30 atoms % silicon), ferrocobalt (Fe_2Co), ferronickel (Fe_2Ni), and various compounds belonging to the metaferrite series, including calcium ferrite, titanium ferrite, ferroferrite (magnetite), ferriferrite (martite and hæmatite), cobaltoferrite, cupri-ferrite, and zinc ferrite. In nearly all cases the dispersion curves show a maximum and minimum within or near the limits of the visible spectrum.

In the case of manganese arsenide and antimonide, iron carbide and ferrosilicon, data were obtained which show the influence of temperature on the Kerr effect. H. M. D.

Decomposition of Complicated Chemical Compounds in a Variable Magnetic Field. GEORGE W. HEIMROD (*Zeitsch. Elektrochem.*, 1913, **19**, 812—816. Compare Rosenthal, A., 1908, ii, 152; Cegielskij, this vol., ii, 752).—The author has repeated the work of Rosenthal of placing a 2·5% solution of sucrose in a variable magnetic field, and, in confirmation of the work of Cegielskij, finds that inversion does not occur. The experiments were conducted over a range of from 200—900 oscillations per second, and at temperatures up to 90°. Further experiments were carried out on the same solutions to which sodium chloride and hydrochloric acid respectively had been added, and in all cases the amount of inversion was identical, whether or no the solution was placed in the magnetic field. It is shown theoretically that there is no reason why such reactions should occur in a magnetic field, and that probably the results of Rosenthal rest upon an error. J. F. S.

An Arrangement for Heating Gases or Vapours to Very High Temperatures. KARL FREDENHAGEN (*Physikal. Zeitsch.* 1913, **14**, 1047).—The apparatus consists essentially of a glass flask, at the centre of which is supported a small tantalum tube 2·5 cm. in length, 0·5 cm. in internal diameter and 0·1 mm. in thickness of wall. The thick copper wires which support the tube at the two ends serve as leads for the current which is employed in heating the tantalum tube. The temperature of this can be readily raised to about 2200°, the current required for this purpose being about 70 amperes.

By means of a side-tube in the neck of the flask, the apparatus can be exhausted, and the flask itself can be readily heated to a moderate temperature in order to vaporise substances which it is desired to subject to the influence of the very high temperature of the tantalum tube. The arrangement has been employed in the investigation of the emission of sodium vapour. H. M. D.

A Method for Electrolytic Heating and Regulation of Thermostats. IRA H. DERBY and JOHN W. MARDEN (*J. Amer. Chem. Soc.*, 1913, **35**, 1767—1769).—Two graphite electrodes, 10 × 10 cm. in

area, or in some cases 10 and 20 cm., and 3·5—13·0 cm. apart, are immersed in the thermostat and connected with a 110-volt source, either alternating or direct, and in series with a relay interrupter connected with the regulator. In a bath of 17—310 litres capacity, the temperature can be kept constant within 0·005—0·025° at temperatures varying from 30—70°.

Copper electrodes also give satisfactory results, but the copper slowly dissolves. T. S. P.

Isothermals of Diatomic Substances and their Binary Mixtures. XIII. Liquid Densities of Hydrogen between the Boiling Point and the Triple Point; Contraction of Hydrogen on Freezing. H. KAMERLINGH ONNES and C. A. CROMMELIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 245—247).—The density of liquid hydrogen increases from 0·07086 at the boiling point ($-252·77°$) to 0·07631 at $-258·27°$. The relationship between the density and temperature is given by the quadratic formula $\rho = a + bT + cT^2$, in which $a = +0·084104$, $b = -0·0002230$, and $c = -0·00002183$.

Contraction occurs on freezing, and at $-262·0°$ the density of solid hydrogen was found to be 0·08077. According to the above formula, the density of liquid hydrogen at the triple point ($-259·2°$) is 0·07709, and on the assumption that the density of solid hydrogen at this temperature does not differ appreciably from that at $-262°$, the contraction on freezing is found to be about 4·8% of the liquid volume. H. M. D.

Molecular Flow and Temperature Change. A Contribution to the Kinetic Theory of Dilute Gases. H. BOLZA, M. BORN, and TH. VON KÁRMÁN (*Chem. Zentr.*, 1913, ii, 1358; from *Nahr. K. Ges. Wiss. Göttingen*, 1913, 221—235).—According to Knudsen, the behaviour of a gas when the dimensions of the space in which it is confined are of the order of the mean free path of the molecules is quite different from that shown by the gas in ordinary circumstances. It is shown that Knudsen's formulæ for molecular flow and molecular heat conduction can be readily deduced from Lorentz's equations for the movement of electrons on the assumption that the conditions obtaining in the case of the gas molecules are analogous. The temperature change which has been found to accompany the molecular flow through porous media can also be accounted for in terms of the general theory, if it is assumed that the gas is adsorbed to some extent by the walls. The observed temperature changes are in approximate agreement with theory in the case of air and carbon dioxide, but considerable divergence is shown by hydrogen. H. M. D.

Specific Heat. MAX TRAUTZ (*Physikal. Zeitsch.*, 1913, **14**, 1176—1178; *Ber. Deut. physikal. Ges*, 1913, **15**, 969—973).—A theoretical paper, in which the author discusses the possibility of explaining the thermal properties of gases on the assumption of a dynamic equilibrium between two isomeric forms, which are mutually transformable at very high velocities. H. M. D.

Experimental Determination of the Specific Heats of Diatomic Gases and Certain Theoretical Conclusions. WILHELM ESCHER (*Ann. Physik*, 1913, [iv], **42**, 761—778).—The specific heats of hydrogen and air have been measured at constant pressure by the mixture method, the apparatus employed being similar to that used by Wiedemann. The specific heat of hydrogen appears to be independent of the temperature between 20° and 100°, the mean value obtained for the molecular heat being $3{\cdot}4219 \pm 0{\cdot}0013$. For air the specific heat was found to be $0{\cdot}23764 \pm 0{\cdot}00035$.

From the equation $M.c_v = M.c_p - 1{\cdot}986$ the author calculates the specific heat ratios to be 1·404 and 1·4047 for hydrogen and air respectively. From experiments made by previous observers on oxygen and nitrogen with the same apparatus, the calculated ratios are 1·3998 and 1·412 respectively. These ratios are shown to be in good agreement with the results obtained in the direct determination of the specific heat ratio.

The specific heat data are further applied in the calculation of the mechanical equivalent, the deviations of the various gases from the ideal state being taken into consideration. The values obtained for the equivalent in ergs are $4{\cdot}202 \times 10^7$ from hydrogen, $4{\cdot}209 \times 10^7$ from air, $4{\cdot}188 \times 10^7$ from oxygen, and $4{\cdot}186 \times 10^7$ from nitrogen.

H. M. D.

Relation Between the Two Specific Heats of Certain Solid Substances. EMIL KOHL (*Chem. Zentr.*, 1913, ii, 742; from *Monatsh. Math. Physik*, 1913, **14**, 197—208).—On the assumption that the van der Waals' equation is applicable to the solid state, and that the variation of the energy of a substance with the temperature is independent of the state of aggregation, it is shown that the difference between the two specific heats can be expressed by $c_p - c_v = 3a\alpha rd/(d_s - d_{sl})$, in which a is the atomic weight, α the coefficient of expansion, r the latent heat of liquefaction, d the density, d_s and d_{sl} the densities of the solid and liquid substance at the melting point.

For a large number of metals and also for sulphur and phosphorus this equation affords values for the difference in the atomic heats which lie between 3 and 4 calories. Since c_p is approximately 6 for the metals, it follows that $c_v = 3$, which is the value obtained for the molecular heat of a monatomic gas. In the case of sulphur and phosphorus, the equation yields $c_p - c_v = 1{\cdot}9$, and this corresponds also with $c_v = 3$.

The author considers that the relationships thus brought to light indicate that the solid and liquid states can be represented by the same equation of condition.

H. M. D.

Anomalies of the Specific Heat of Certain Alloys OSKAR RICHTER (*Ann. Physik*, 1913, [iv], **42**, 779—795. Compare this vol., ii, 184).—According to the theory put forward by Richarz to explain the properties of elements in the solid state, an element should have the greatest specific heat in that modification in which its density is smallest. In order to ascertain whether this relation-

ship is applicable to metallic alloys, the author has examined the data previously obtained (*loc. cit.*) for the specific heats of a series of alloys of bismuth and tin and of bismuth and lead.

In the case of the bismuth–tin alloys, the observed densities are smaller than those calculated according to the mixture rule, whilst the observed specific heats are greater than the calculated values. This is supposed to be in agreement with the requirements of the above-mentioned theory.

On the other hand, the required relationship is not satisfied at all by the experimental data for the bismuth–lead alloys, and the anomalies exhibited in this case are attributed to the formation of a chemical compound. From the position of the maximum deviation of the values of the density and specific heat from those calculated from the mixture rule, it would appear that this compound corresponds with the formula BiPb.

Further observations are described which show that the specific heat of bismuth–lead alloys is to some extent dependent on the previous thermal treatment, and on the rate at which solidification occurs when the alloy is cast. These variations aro discussed from the point of view of Richarz's theory. H. M. D.

Compressibility and Differences of Specific Heats of Liquids. THADÉE PECZALSKI (*Compt. rend.*, 1913, **157**, 770—773).—A mathematical discussion of the relationship between the specific heats of a liquid at constant volume and constant pressure, and its coefficient of dilatation. W. G.

Latent Heat of Fusion. GUSTAV TAMMANN (*Zeitsch. physikal. Chem.*, 1913, **85**, 273—296).—The latent heat of fusion of isotropic and anisotropic substances is considered theoretically. It is shown that the heat of fusion r can be represented by the equation $r = A_a + A_i + \Delta E + \Delta\pi + \Delta x W_a$, where A_a and A_i represent the work performed against external and internal forces respectively, ΔE the energy difference of the molecule in isotropic and anisotropic conditions, and $\Delta\pi$ the difference of the potential energy between the two molecular orders, W_a the heat of association, and Δx the change of the association factor on melting. At the maximum melting point on the fusion curve, the volume difference between the isotropic and anisotropic phases disappears, and consequently the internal and external work on melting, hence $r_{p.(max.)} = \Delta E + \Delta\pi$.

It is shown that this expression cannot be evaluated from the knowledge of the diagram of condition. The expression is theoretically considered and tested in known cases. J. F. S.

Determination of Melting Point by the Thermometer Bulb Method. ROBERT MELDRUM (*Chem. News*, 1913, **108**, 223—224).—The varying results obtained with the thermometer bulb method for the determination of the melting point of fats and waxes have led to the general opinion among analysts that the melting point is affected by the length of time the fat is kept molten, and also by rapid cooling. The author's experience is not

in agreement with this opinion, the varying results being ascribed to the defective experimental methods used. Minute details are given of the method which should be used in coating the bulb with fat; also with respect to the influence of the thickness of the coating, of the part played by viscosity, and of the rate of heating.

In fifty-nine determinations made by the author the maximum variation does not exceed 0·6°. T. S. P.

The *T-X*-Figure of the System Benzene-Quinine. J. W. VAN IterSON-ROTGANS (*Chem. Weekblad*, 1913, **10**, 920—939).—An investigation of the melting points and the vapour tension at constant temperature of a large number of mixtures of benzene and quinine, illustrated by curves and diagrams of the apparatus employed. A. J. W.

Vapour-pressure Measurements and Thermometry at Low Temperatures. H. VON SIEMENS (*Ann. Physik*, 1913, [iv], **42**, 871—888).—The vapour pressures of liquid carbon disulphide, carbon dioxide, oxygen, and nitrogen have been measured in a closed apparatus constructed entirely of glass, and similar in form to that described by Stock and Nielsen (A., 1906, ii, 521). In all cases the observations can be satisfactorily represented by Nernst's formula, the actual formula for carbon disulphide being $\log p = -1578 \cdot 8/T + 1 \cdot 75 \log T - 0 \cdot 003874T + 4 \cdot 67948$; for carbon dioxide, $\log p = -1378 \cdot 3/T + 1 \cdot 75 \log T - 0 \cdot 0051T + 6 \cdot 9484$; for oxygen, $\log p = -399/T + 1 \cdot 75 \log T - 0 \cdot 01292T + 5 \cdot 0527$; for nitrogen, $\log p = -323 \cdot 5/T + 1 \cdot 75 \log T - 0 \cdot 01250T + 4 \cdot 7306$; and for solid nitrogen, $\log p = -345 \cdot 6/T + 1 \cdot 75 \log T - 0 \cdot 00696T - 4 \cdot 7306$. The vapour-pressure data are applied to the calculation of the latent heat of vaporisation, the numbers thus obtained being in all cases in satisfactory agreement with the experimental values.

Platinum resistance thermometers were employed in the determination of temperatures, the data recorded by Onnes and Clay being made the basis of the scale of temperatures. It is shown that the variation of the resistance of platinum with the temperature, as represented by the data in question, can be represented by means of a cubic equation for temperatures above 100° (absolute). By means of this equation and Nernst's empirical reduction formula, it is possible to bring the readings of any platinum resistance thermometer into line with the standard scale by observations at four temperatures.

Convenient constant temperature baths for low temperature work, and particularly for vapour-pressure measurements, are also described in the paper. H. M. D.

Vapour Pressures of Substances of Low Critical Temperature at Low Reduced Temperatures. I. Vapour Pressures of Carbon Dioxide between −160° and −183°. H. KAMERLINGH ONNES and SOPHUS WEBER (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 215—227).—The vapour-pressure measurements between 1 mm. and 0·01 mm. of mercury were made with the aid of Knudsen's

hot-wire gauge, those between 0·01 and 0·001 mm. by means of Knudsen's absolute manometer. The vapour pressure increases from 0·008 barye at $-183·0°$ to 1·310 barye at $-167·04°$. The pressures calculated from Nernst's formula, using the constants determined by Falck (A., 1908, ii, 662), are in good agreement with the observed values. H. M. D.

Vapour Pressures of Certain Univariant Systems. I. Na_2CO_3 and H_2O. A. F. Gerasimov (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1655—1668).—The author has devised an apparatus suitable for the measurement of the vapour pressures of saturated solutions, which (1) admits of spontaneous change in the volume of the gaseous phase, (2) yields results the accuracy of which corresponds with that of the temperature measurements, and (3) allows of the verification at any moment of the completeness of removal of the air from the apparatus. For the detailed construction of the latter the original must be consulted.

By means of this apparatus the vapour pressures of saturated sodium carbonate solutions were measured at a series of temperatures ranging from 33·9° to 101°. The numbers obtained are expressed, for temperatures varying from 37·8° to 101°, very nearly by the equation: $\log P = 8·0684842 + 50[\log (T - 80·293) - \log T]$. For the boiling point of the saturated solution under normal pressure, extrapolation gives 104·8°, the temperature given in Landolt's tables being 105°. The author's numbers are in all cases appreciably lower than those given by Speranski (A., 1909, ii, 378; 1911, ii, 1065) for the temperature range 33·9—49·95°. T. H. P.

Attainment of Constant Temperatures. A. F. Gerasimov (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1668—1674).—By means of mixtures in different proportions of two liquids which do not exhibit maxima or minima of vapour pressure, all temperatures intermediate to the boiling points of the constituents may be attained. But in order that any such temperature may be maintained constant for a length of time, it is necessary that the apparatus enclosing the boiling mixture be completely isolated from the atmosphere. On the other hand, the avoidance of bumping necessitates the continuous supply to the boiling mixture of a small quantity of air. The author has constructed an apparatus which satisfies these requirements. The flask containing the boiling liquid is connected with the constant temperature space by means of two tubes traversing the corks, one tube for the passage of vapour from the flask to the space, and the other for the return of condensed liquid below the surface of the boiling mixture. The upper part of the constant temperature space communicates with a condenser, which condenses the vapour and passes it as liquid into a wide tube, which becomes narrower before it enters the boiling flask to reach below the surface of the liquid; fitted in the shoulder of this tube is a conical piece of brass gauze, which causes the condensed liquid flowing into the flask to act in the same manner as the mercury in a Sprengel pump, so that a chain

of air and liquid bubbles passes into the flask. All the connexions are made with corks sealed with mercury. The apparatus functions well, no matter whether the liquid mixture be boiled slowly or rapidly, and, using mixtures of chloroform and carbon tetrachloride, the temperature in the constant temperature space could be kept at 63·5—63·6° or 66·95—67·1° for some hours, the flask being heated by an ordinary burner.

With such an apparatus, constancy of temperature depends on constancy of gas-pressure, and good results are obtained only after more or less perfect establishment of thermal equilibrium in the apparatus, this necessitating communication with the atmosphere for some time. These inconveniences were overcome by means of a gas regulator in the form of a U-tube manometer connected with the space between the lower end of the condenser and the boiling flask. One limb of the manometer contained an iron wire in continual contact with the mercury, and the other a similar wire joined to a platinum disk situate just above the surface of the mercury. These wires are connected with an electromagnetic apparatus controlling the gas-tap. By such means both the pressure and the temperature within the apparatus may be constrained to vary within definite limits, and in order to make these as narrow as possible, the thermal inertia of the apparatus must be diminished as far as possible. This may be effected by standing the flask on an iron tripod with a copper gauze, and by leaving it quite uncovered except for a small asbestos cup fitted to the upper part to protect the vapours from superheating. A regular oscillation of the temperature over 0·05° is thus attainable. T. H. P.

An Improved Type of Calorimeter, to be Used with Any Calorimetric Bomb. J. A. Riche (*J. Amer. Chem. Soc.*, 1913, 35, 1747—1750).—The calorimetric bomb is immersed in water contained in a Dewar vacuum cup standing on a wooden base. The cup and base are surrounded by an oak box, lined with pressed cork; on the under side of the cover, in addition to the cork, is glued a piece of felt, of such a thickness that a tight joint is effected with the top of the vacuum cup. There are appropriate holes in the cover for the introduction of a thermometer, of electric leads for ignition purposes, and of a screw-propeller stirrer for the water surrounding the bomb. T. S. P.

Relation Between the Heat of Formation of Binary, Liquid Mixtures and their Composition. Émile Baud (*Compt. rend.* 1913, 157, 849—850).—The heat of mixture of two liquids, without chemical action on one another, can be expressed by the equation $q=kx(1-x)$, where q is the amount of heat, x the fraction of a gram-molecule of one constituent, and $(1-x)$ the fraction of a gram-molecule of the other constituent, k being a constant. Results are given for a mixture of *cyclo*hexane and *s*-dibromoethane, which verify this equation, and similar results have been obtained with other mixtures. The value of k lies between 1·32 and 1·35 for the mixture quoted. W. G.

Heats of Formation of Additive Organic Compounds. II. Racemates (Dimethyl Tartrate). BARTOLO L. VANZETTI (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 328—332. Compare this vol., ii, 296).—The following heats of solution in aqueous alcohol have been determined: Methyl *d*-tartrate, −5·392 Cal.; mixture of methyl *d*- and *l*-tartrates, −5·396 Cal.; methyl racemate, −12·350 (−12·143 to −12·613) Cal. Hence, heat of formation of the racemate (from 2 active mols.) is +1562 cals. T. H. P.

Apparatus for the Measurement of the Density and Viscosity of Gases. M. HOFSÄSS (*Chem. Zentr.*, 1913, ii, 1353; from *J. Gasbeleuchtung*, 1913, **56**, 841—843).—The apparatus has been designed for comparative observations on the rate of effusion and on the rate of flow through a capillary tube. The gas reservoir consists of a wide cylindrical tube connected above and below with narrow tubes provided with efficient taps. The tube at the lower end communicates with an open manometer tube containing a suitable liquid, whilst the tube at the upper end serves for the introduction of gas into the apparatus and communicates through a side-tube with a perforated diaphragm, which can be shut off from the reservoir by a tap. In carrying out an experiment, this tap is opened, and the time required for the fall of the manometer liquid over the distance fixed by two marks on the manometer tube is measured by means of a stop-watch. When the apparatus is to be used for viscosity measurements, the perforated diaphragm is replaced by a suitable capillary tube. H. M. D.

Vaporisation. VII. HANNS VON JÜPTNER (*Zeitsch. physikal. Chem.*, 1913, **85**, 1—61. Compare A., 1908, ii, 663, 810; 1909, ii, 21; 1910, ii, 583, 689; 1912, ii, 829).—A theoretical paper, in which the author shows that the formulæ

$$(1)\ (D_{\text{liq.}} + D_{\text{vap.}})/2D_k = D_0/2D_k(1 - T/T_k) + T/T_k$$

and

$$(2)\ (D_{\text{liq.}} - D_{\text{vap.}})/2D_k = D_0/2D_k(1 - T/T_k)^{1/3}$$

represent the relationship between the density of a liquid and its vapour with the critical density, and in both equations the quantity $(D_0/2D_k)$ is a constant. These expressions are tested on a large number of published observations, and it is shown that substances which have unchanged molecular size over the range of temperature examined have also the value $D_0/2D_k$ constant. Those substances the molecular size of which is changed have varying values of the constant. A number of new equations for the heat of vaporisation for ideal liquids are deduced. J. F. S.

[Determination of] The Densities of Certain Dilute Aqueous Solutions by a New and Precise Method. ARTHUR B. LAMB and R. EDWIN LEE (*J. Amer. Chem. Soc.*, 1913, **35**, 1666—1693).—The authors have improved the submerged sinker method for the determination of densities of liquids, and claim to have attained an accuracy of less than one unit in the seventh decimal place. The

sinker consists of an inverted Jena flask of about 250 c.c. capacity, weighted with mercury, and containing a fixed, vertical, soft iron rod, so that it can be moved up and down in the liquid by means of an electromagnetic arrangement; a platinum point is fused into the sealed neck of the flask. The method of procedure was to place platinum weights on the sinker until it just barely floated, and then regulate the electromagnet so that the sinker was pulled down and the platinum point just touched a platinum saucer at the bottom of the vessel containing the liquid, a special microscope being arranged to observe the point of contact. The current through the electromagnet having previously been calibrated in terms of weight, the weight of the sinker when just floating could bo found, and hence the density of the liquid. Due precautions were taken to keep the temperature constant by means of a thermostat, and the corrections for changes in the barometric pressure and for other variations causing errors were applied.

The densities of 0·0001—0·01*N*-solutions of salts of sodium, potassium, ammonium, lithium, magnesium, and zinc were determined relative to that of water at 20·004°, and the volume changes occurring on solution calculated. The variations in these volume changes indicate, in general, a progressively increasing compression as the dilution increases, but an approximate constancy is reached at dilutions where the electrolytic dissociation is practically complete. Of the solutions studied, sodium carbonate alone presents an anomalous behaviour in this particular, for in very dilute solution the contraction becomes less rather than greater. This anomaly can be explained on the basis of the unusual contraction which occurs during the neutralisation of carbonic acid.

T. S. P.

Volume Changes of Amalgams. J. WÜRSCHMIDT (*Ber. Deut. physikal. Ges.*, 1913, **15**, 1027—1036. Compare this vol., ii, 101).—Further experiments have been made on volume changes in amalgams. In the case of zinc amalgams, volume changes occur at temperatures below the melting point which are presumably due to changes in structure. Bismuth amalgam, of the composition BiHg, contracts at the melting point, and thus behaves like pure bismuth, but the volume contraction in the case of the amalgam begins at temperatures considerably below the melting point.

H. M. D.

The Expansion Pressures of Normal Liquids. L. GAY (*Compt. rend.*, 1913, **157**, 711—714).—The author has verified the formula $\log \pi = \log RT/(V-b) + b/(V-b) - (EL+PV-RT)/RT$ (compare this vol., ii, 382, 388) for normal pentane, hexane, heptane, octane, βε-dimethylhexane, ethyl bromide, bromobenzene, and ethyl ether. Using Young's values, he has calculated the ratio between (1) the critical molecular volume, (2) tho theoretical molecular volume, and the co-volume *b*, and finds these ratios to be constant for these substances, thus verifying his law of the corresponding states.

W. G.

The Weight of a Falling Drop and the Laws of Tate. XIII. The Drop Weights of Aqueous Solutions and the Surface Tensions Calculated from them. J. LIVINGSTON R. MORGAN and GEORGE A. BOLE (*J. Amer. Chem. Soc.*, 1913, **35**, 1750—1759).—The authors show that the Morgan drop-weight apparatus can be satisfactorily used for the determination of the surface tensions of salt solutions, and when so used gives results which are in excellent agreement with the best results found by other standard methods.

By the study of the solutions of some twenty inorganic salts, one equivalent of each being dissolved in 1000 grams of water, it was shown that Valson's law (that the surface tension of normal solutions of salts is identical) is untrue, and that the results on which he based it are incorrect. T. S. P.

The Weight of a Falling Drop and the Laws of Tate. XIV. The Drop Weights of Aqueous Solutions of the Salts of Organic Acids. J. LIVINGSTON R. MORGAN and WALTER W. MCKIRAHAN (*J. Amer. Chem. Soc.*, 1913, **35**, 1759—1767).—From the determination of the drop weights and surface tensions of semi-normal solutions of thirty different salts of organic acids, at different temperatures, the change in surface tension with the temperature is found to be linear, within the limits of temperature studied.

Some salts raise the surface tension of water, whilst others lower it, which facts contradict Valson's generalisation that all normal solutions of salts at the same temperature have identical values for the surface tension.

The acids, citric, tartaric, and oxalic, lower the surface tension of water, so that hydrolysis in solutions of their salts would tend to lower the surface tension.

Generally, salts of the same acid show a marked agreement in their values for the surface tension at the same temperatures, but there are exceptions, for example, with barium and copper salts.

The surface tension of a solution of two salts, one of which raises and the other lowers the surface tension of water, is an additive property of the two separate solutions, provided no chemical action takes place, and that the separate values of the surface tension are not very far removed from that of water. If one of the solutes causes a much larger effect than the other, the value for the mixture lies closer to the one with the greater effect.
T. S. P.

Adsorption of Electrolytes. KNUD ESTRUP (*Chem. Zentr.*, 1913, ii, 1102; from *Over. K. Danske. Vidensk. Selsk. Vorhand.*, 1913, 13—45).—Methods are described for the estimation of the purity of adsorbent substances, such as the different forms of animal charcoal, in which hydrochloric acid or potassium hydroxide is added until the positive and negative ions of certain neutral salts (ammonium nitrate, iodate, dichromate) are equally adsorbed by the charcoal. The amount of acid or alkali required per 2 grams of adsorbent when shaken with 100 c.c. of solution affords a measure of the impurity.

The adsorption of electrolytes from solutions containing two salts with a common cation or anion has also been investigated. In general, the adsorption of a particular ion is diminished when a second, similarly charged ion is added to the solution, but several exceptions have been observed. For example, the hydrogen and iodate ions are more readily absorbed in presence of the ammonium and sulphate ions respectively. In the case of two ions of similar sign but different valency, it is found that the more highly charged ion has the greater influence in lowering the adsorption tendency.

From observations on negative adsorption, the author has deduced a value for the degree of dispersity of charcoal. On the assumption that the particles are cubical, this is of the order $6 \cdot 10^5$ to $6 \cdot 10^7$.

H. M. D.

Adsorption of Colloidal Ferric Hydroxide. NILS CARLI (*Zeitsch. physikal. Chem.*, 1913, **85**, 263—272).—Experiments are made on the adsorption of ferric hydroxide by animal charcoal and kaolin. It is shown that the amount of adsorption by animal charcoal is independent of the volume of sol and the amount of colloid present, but is directly proportional to tho weight of the charcoal. Consequently the adsorption does not follow the usual adsorption law: $\lambda = v/m \log_e(a/a-x)$. Kaolin exerts only the slightest adsorption on ferric hydroxide sols. J. F. S.

Dependence of the Capillary Constant of Water and of Alcohol–Water Mixtures on the Temperature. MAX REINHOLD (*Ber. Deut. physikal. Ges.*, 1913, **15**, 903—912).—The data recorded were obtained from measurements of the wave-length of the capillary waves generated on a freshly prepared surface of the liquid by a vibrating tuning-fork. For the five alcohol–water mixtures investigated between 5° and 65°, the influence of temperature on the surface tension can be represented by a linear equation $\alpha_t = \alpha_0(1 - kt)$. The temperature-coefficients observed for the mixtures containing 10, 30, 50, 70, and 94% by weight of alcohol are respectively $0 \cdot 0^3 206$, $0 \cdot 0^3 136$, $0 \cdot 0^3 105$, $0 \cdot 0^4 98$, and $0 \cdot 0^4 79$.

In the case of water, the data obtained at temperatures between 0° and 85° give rise to a more or less sinuous curve when the surface tension is plotted against temperature. H. M. D.

The Idea of Osmotic Pressure and its Application to Colloidal Solutions. ARRIGO MAZZUCCHELLI (*Gazzetta*, 1913, **43**, ii, 404—422).—A theoretical discussion. R. V. S.

The Two Roots of Ostwald's Equation. ARRIGO MAZZUCCHELLI (*Gazzetta*, 1913, **43**, ii, 423—428).—The author discusses the significance of the negative root of the equation $\alpha^2/(1-\alpha)V = K$.

R. V. S.

Measurement of the Fluidity of Solutions. G. MUCHIN (*Zeitsch. Elektrochem.*, 1913, **19**, 819—821).—Determinations of the fluidity of the following binary mixtures are given. Benzene–

paracetaldehyde, paracetaldehyde–acetic acid, benzene–acetone, acetone–*n*-hexane, acetone–nitrobenzene, acetone–ethyl alcohol, acetone–water, *iso*amyl alcohol–hexane, *iso*amyl alcohol–benzene, *iso*amyl alcohol–ethyl alcohol, benzene–nitrobenzene, benzene–acetic acid, benzene–ethyl alcohol, paracetaldehyde–ethyl alcohol, and paracetaldehyde–nitrobenzene. The determinations were mostly carried out at 20° by means of a closed Ostwald viscometer. The object of the work was to test the formula $\phi = \phi_1 a + \phi_2(1-a)$ (Drucker and Vassel, A., 1911, ii, 373). It is shown that generally the formula does not hold, but the author regards the work as preliminary, and is of the opinion that the formula is generally applicable provided no complications occur in the mixtures. J. F. S.

Economic Lixiviation. P. J. H. VAN GINNEKEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 201—214).—A theoretical paper in which the author discusses the relative merits of discontinuous, semi-continuous, and continuous lixiviation with reference to the economy of the solvent. H. M. D.

Solubility in the Solid State between Nitrates, Sulphates, and Carbonates at High Temperatures. MARIO AMADORI (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 332—337).—The author has investigated the melting-point curves of the systems $LiNO_3$–Li_2SO_4, $NaNO_3$–Na_2SO_4, KNO_3–K_2SO_4, $LiNO_3$–Li_2CO_3, $NaNO_3$–Na_2CO_3, KNO_3–K_2CO_3. The results obtained differ from those yielded by the sulphate–carbonate systems (A., 1912, ii, 917), the mutual solubility in the solid state of nitrate and sulphate or nitrate and carbonate being either zero or very small. The nitrates crystallise with the carbonates and with the sulphates in simple eutectics consisting almost exclusively of nitrate at temperatures only 3—10° below those at which the nitrates solidify. As with sulphates and carbonates, so also with nitrates and sulphates or nitrates and carbonates, no formation of compounds occurs on solidification or at lower temperatures. T. H. P.

Cause of the Abnormal Linear Velocity of Crystallisation of Supercooled Crystalline Substances. K. P. GRINAKOVSKI (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1210—1248. Compare Tammann, A., 1911, ii, 376).—The author has devised an apparatus for the determination of the molecular surface energy of supercooled, viscous, crystalline substances, and has measured the surface energy and density of benzophenone, erythritol, acetanilide, 3 : 4-dinitrophenol, *m*-chloronitrobenzene, *m*-bromonitrobenzene, chloroacetic acid, antipyrine, sodium thiosulphate, ferric nitrate, and benzil. With all these compounds, the linear velocity of crystallisation follows an abnormal course, the region of constant velocity being absent.

The results obtained show the inaccuracy of Tammann's supposition that the character of this velocity curve is influenced solely by phenomena of polymerisation, and indicate that abnormalities are dependent on: (1) the influence of admixtures intro-

duced during recrystallisation; (2) the influence of removal of heat (crystallisation in capillaries); (3) the influence of decomposition during fusion; (4) the influence of polymorphous modifications.

T. H. P.

Influence of the Degree of Supersaturation of a Solution on the External Form of Crystals of Alum Separating from It. A. SCHUBNIKOV (*Bull. Acad. Sci. St. Pétersbourg*, 1913, 817—828).—The object of the author's investigations was to test experimentally Johnsen's view ("Wachstum und Auflösung der Kristalle," Leipzig, 1910) that with every degree of supersaturation of a solution corresponds its own perfectly definite crystalline form.

Experiments made with alum show that diminution of the extent to which the solution is supersaturated is accompanied by enhancement of the internal, and by lowering of the external, symmetry of the crystals; that is, highly supersaturated solutions yield non-homogeneous crystals, which include mother-liquor, but are remarkably regular in appearance, whilst slightly supersaturated solutions give homogeneous, transparent crystals of unsymmetrical shape.

Further, decrease in the degree of supersaturation occasions increase in the number of faces of the crystals, whereas, according to the conclusions drawn by Andréev (A., 1908, ii, 475), the opposite should be the case.

No simple law could be found connecting change in the rate of growth of the crystals with change in the extent of supersaturation of the solution. Diminution in the degree of supersaturation is accompanied by rounding-off of the crystals, that is, by decrease of the surface area per unit weight; this conclusion is indicated by the habit of the crystals, and confirmed by actual measurement.

T. H. P.

Relation between the Crystal Symmetry of the Simpler Organic Compounds and their Molecular Constitution. II. WALTER WAHL (*Proc. Roy. Soc.*, 1913, *A*, **89**, 327—339. Compare A., 1912, ii, 1044).—The author has investigated the crystalline form of a large number of organic substances, most of which melt at low temperatures, including the unsaturated aliphatic hydrocarbons, the simpler oxygen, sulphur and halogen compounds of carbon, and the simpler aromatic hydrocarbons. The optical properties are described in detail, and in many cases the probable crystalline form is inferred from the optical behaviour. No general conclusions are drawn from the detailed observations. H. M. D.

Influence of Chemical Constitution on the Thermal Properties of Binary Mixtures. III. PAUL PASCAL and LÉON NORMAND (*Bull. Soc. chim.*, 1913, [iv], **13**, 878—889. Compare this vol., ii, 292).—In the previous papers it has been shown that molecular symmetry in the two constituents determines the existence of a continuous series of mixed crystals, but that this property disappears when one of the constituents has an unsymmetrical aliphatic chain. In order to determine the influence of the nucleus

on the tendency to syn-crystallisation, melting-point curves have been determined for binary mixtures, including constituents in which the nuclei have been loaded in various ways. Tables and graphs are given for the following mixtures: (1) stilbene and *p*-dimethoxystilbene, (2) azobenzene and azotoluene, (3) stilbene and azotoluene, (4) azobenzene and dimethoxyazobenzene, (5) stilbene and aminoazobenzene, (6) azobenzene and azonaphthalene, (7) stilbene and azonaphthalene, (8) azobenzene and benzeneazonaphthalene, (9) benzylidene-α- and benzylidene-β-naphthylamines, (10) tetraphenylethylene and tetraphenylsilicon. The following general conclusions are drawn. Mixtures of two substances separately symmetrical furnish mixed crystals in all proportions when both have the same nuclear structure, and this property is not destroyed by symmetrical substitution. Two substances which are separately symmetrical show isodimorphism when their nuclei are different. Asymmetry of structure in the central chain produces isodimorphism, independently of the nuclear structure, and asymmetry of the nuclear structure produces a similar effect. With increasing constitutional difference and reciprocal asymmetry of the components of a binary mixture, isomorphism (and the spindle-shaped melting-point curves associated with this) undergoes a regular involution, isodimorphism becomes marked, and the areas of syn-crystallisation increase. T. A. H.

The Relationship between Colloid Coagulation and Adsorption and the Velocity of Coagulation. HERBERT FREUNDLICH and N. ISHIZAKA (*Zeitsch. physikal. Chem.*, 1913, **85**, 398—400. Compare this vol., ii, 486).—It is shown that the auto-catalytic coagulation which was expressed (*loc. cit.*) by the expression:

$$k = 1/z^2(1+b)\{b/(1+b)[\log_{\text{nat.}}(1+bx) - \log_{\text{nat.}}(1-x)] + x/1-x\}$$

can be expressed equally well by the expression:

$$k' = 1/(1-b')z^2\{\log_{\text{nat.}}(1+b'x) - \log_{\text{nat.}}(1-x)\}.$$

the constants in both cases being equally satisfactory. J. F. S.

The Distribution of a Suspended Powder or of a Colloidally Dissolved Substance between Two Solvents. WILHELM REINDERS (*Kolloid. Zeitsch.*, 1913, **13**, 235—241*).—It is shown that when a liquid (1), in which a finely divided solid substance (3) is suspended, is shaken up with a second immiscible liquid (2), the resulting distribution is determined by the surface tensions at the surfaces of separation of the three phases. If $\sigma_{2\cdot3} > \sigma_{1\cdot2} + \sigma_{1\cdot3}$, the solid will remain suspended in the first liquid. If $\sigma_{1\cdot3} > \sigma_{1\cdot2} + \sigma_{2\cdot3}$, the solid will pass into the second liquid. Thirdly, if $\sigma_{1\cdot2} > \sigma_{2\cdot3} + \sigma_{3\cdot1}$, or if none of the surface tensions is greater than the sum of the other two, the solid will collect in the surface layer separating the two liquids.

Experiments with different solids and pairs of liquids have shown that all three cases are met with in practice, and it is

* and *Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 379—388.

possible to effect a separation of solid substances in certain cases on the basis of the differences which they exhibit in their mode of distribution between certain pairs of liquids. If, for instance, a mixture of galena and quartz is shaken with water and *iso*butyl alcohol, the quartz remains suspended in the aqueous layer, whilst the galena is found at the surface of separation. The observations made with water as the one liquid, and paraffin oil, amyl alcohol, carbon tetrachloride, benzene, and ethyl ether as the other, indicate that silicates, sulphates, and carbonates of the light metals generally remain suspended in the water layer, whilst compounds of the heavy metals and non-metallic elements, such as carbon, sulphur, and selenium, pass into the surface of separation or into the non-aqueous liquid. Of the non-aqueous solvents examined, paraffin oil and amyl alcohol represent those which take up the suspended substance most readily.

The behaviour of a colloidal solution is in all probability dependent on the size of the colloidal particles, but experiments with colloidal gold solutions indicate that the phenomena of distribution are similar to those met with in the case of solid suspensions.

If a red or reddish-violet colloidal solution of gold in water is shaken with *iso*butyl alcohol, amyl alcohol, benzene, carbon tetrachloride, carbon disulphide, or ethyl ether, the gold passes into the surface layer of separation, and forms a blue deposit. If, on the other hand, the yellowish-brown solution of gold in amyl alcohol, prepared by reduction of the chloride with phosphorus, is shaken with water, the colloidal gold remains suspended in the amyl alcohol layer. Other experiments show in a similar manner that the behaviour of colloidal gold is more or less dependent on its degree of dispersity. The presence of a protective colloid, such as gum arabic, is also found to have an appreciable influence on the phenomena of distribution.

In addition to gold, colloidal solutions of silver, ferric hydroxide, arsenious sulphide, molybdenum trioxide, selenium, tellurium, and carbon have been examined. H. M. D.

New Electrical Method of Preparing Aqueous Colloidal Solutions of Metals. H. MORRIS-AIREY and S. H. LONG (*Proc. Univ. Durham Phil. Soc.*, 1913, **5**, 68—70).—The method involves the use of a high frequency alternating arc, a suitable generator being provided by the Poulsen arc, as used in wireless telegraphy. The discharger circuit, which contains an arc lamp, designed so as to allow of the arc being struck under water, is connected up to two points on the inductance of the oscillatory circuit. By varying the inductance and capacity of the oscillatory circuit and introducing various capacities and inductances into the discharger circuit, the electrical conditions of the discharge can be readily varied between wide limits. It is claimed that the new method possesses marked advantages over the methods described by Bredig and Svedberg, and, in general, only a few seconds are required for the preparation of colloidal solutions of different metals. By varying the conditions of discharge, it has been found that solutions of different colours

can be obtained in the case of several of the metals submitted to examination. H. M. D.

Protective Colloids. Starch as Protective Colloid. I. Colloidal Silver. ALEXANDER GUTBIER and E. WEINGÄRTNER (*Koll.-chem., Beihefte*, 1913, 5, 211—243).—The behaviour of starch as a protective colloid towards colloidal silver has been examined in detail.

The solutions obtained by reduction with hydrazine and with sodium hyposulphite are very similar in their properties, although the rapidity with which the latter reacts and the nature of its oxidation products are responsible for certain anomalies observed with colloidal solutions obtained by this method of reduction. The coagulating influence of electrolytes diminishes in the order: sulphuric acid, barium chloride, magnesium sulphate, ammonium carbonate, sodium hydroxide in the case of the solutions reduced by hydrazine; and in the order: barium chloride, sulphuric acid, magnesium sulphate, sodium carbonate, sodium hydroxide for solutions reduced by sodium hyposulphite. In general, those electrolytes which accelerate the ageing of the starch solutions increase the rate of coagulation, whilst those which retard the coagulation of pure starch solutions have a similar influence on the silver starch sols.

The protective action of starch solutions prepared at 100° and at 120° is practically the same, although the stability of dilute silver solutions is somewhat greater for the clear starch solutions which are obtained at the higher temperature.

The starch silver sols are coagulated on the addition of alcohol, and under the influence of an electrical field, their behaviour is similar to that exhibited by starch solutions, and quite different from that of colloidal silver solutions in the absence of starch.

Although hydrogen peroxide is readily decomposed by colloidal silver, it is found that the catalytic effect is greatly diminished in presence of starch. In the case of dilute solutions of hydrogen peroxide, there is a small initial evolution of oxygen, but the reaction quickly ceases. With concentrated hydrogen peroxide solutions, the anti-catalytic influence of the starch is not sufficient to stop the reaction, and this is attributed to the hydrolytic action of the hydrogen peroxide on the starch.

Other experiments show that starch solutions have a reducing action on silver nitrate when the reaction mixture is exposed to light, but this change takes place too slowly to have any appreciable influence on the reduction which occurs in presence of hydrazine or sodium hyposulphite. H. M. D.

Protective Colloids. Starch as Protective Colloid. II. Colloidal Gold. ALEXANDER GUTBIER and E. WEINGÄRTNER (*Koll-chem. Beihefte*, 1913, 5, 244—268).—Similar experiments to those described in the previous paper have been carried out with colloidal gold solutions. In general, the protective influence of the starch is of the same nature as in the case of colloidal silver solutions.

The concentration of the starch has an appreciable influence on the colour of the solutions obtained by reduction with hydrazine, a series of comparative experiments showing that the blue colour becomes darker and shades off towards violet as the concentration of the starch is increased.

Towards electrolytes, the protective influence of starch is closely similar to that found in the case of colloidal silver.

The reducing action of starch solutions on gold chloride has also been examined. These experiments show that colloidal gold is produced in these circumstances, the colour changing from red to blue as the reaction proceeds. The coagulation phenomena observed with the gold sols prepared in this way are very similar to those exhibited by the sols obtained by reduction with hydrazine in presence of starch. In presence of alkali, the reducing action of starch on gold chloride is considerably accelerated. H. M. D.

Chemical and Physico-chemical Properties of Liquids Expressed from Striated and Plain Muscle. III. Variations of Volume During Certain Colloidal Processes. FILIPPO BOTTAZZI and E. D'AGOSTINO (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 307—315. Compare this vol., i, 1132).—Dilatometric measurements made with dry gelatin in water show that imbibition of gelatin is accompanied by contraction of volume, which is at first very rapid, but subsequently falls off. The similar contraction proceeding with dry, granular myosin takes place much more slowly than with gelatin. In general, acids and bases occasion increase in the imbibition of colloids. and it is found that myosin which has imbibed the maximum proportion of water undergoes further diminution of volume in presence of small amounts of lactic or hydrochloric acid; this diminution takes place at first rapidly, and then more slowly, and increases with the proportion of lactic acid present. On the other hand, addition of an alkali invariably results in increase in volume.

These results are explained on the assumption that when a protein is in presence of an aqueous acid or alkali solution free from salt, three processes occur: imbibition of the colloid, solution of the latter in the case when it swells to an illimitable extent, and formation of a salt of the protein with the acid or base. The first two of these are accompanied by contraction and the last by expansion, the net result depending on the predominance of one or the other of these changes. T. H. P.

The Structure of Gels. RICHARD ZSIGMONDY (*Physikal. Zeitsch.*, 1913, **14**, 1098—1105).—The structure of gels is discussed with special reference to the two principal theories which have been put forward. In many cases the structure revealed by the ultramicroscope is distinctly favourable to the micellary theory, but other cases are known in which the heterogeneity exhibited by the gels is such as to lend support to the opposing theory advocated by Quincke and Bütschli.

The properties of silica, obtained by dehydrating silicic acid

jelly over sulphuric acid, are described. The heterogeneity of the structure in this case is such that the clear, transparent silica appears to be optically homogeneous, although the substance is undoubtedly porous, the volume of the free space amounting to 30—60% of the total volume.. The water which is absorbed by this extremely fine capillary network has an appreciably lower vapour pressure than water in bulk, and according to van Bemmelen's measurements of the vapour pressure at different stages during the absorption and removal of water, it appears that the curves corresponding with the two processes diverge appreciably. Similar measurements have been carried out with a silicic acid gel during the absorption of water, ethyl alcohol, and benzene. In all three cases the vapour-pressure curves are of the same type and quite similar to that which represents van Bemmelen's results. The data are employed to calculate the mean radius of the capillary tubes, the same value, $r=2 \cdot 6 \mu\mu$, being obtained from the three sets of observations. This concordance indicates that the deviations of the vapour pressures from the normal values are due to capillary effects, and that the degree of heterogeneity of the gel can be determined with considerable exactitude. H. M. D.

Equation of Condition, Equilibrium Diagram, and Association Hypothesis. LÉON SCHAMES (*Ber. Deut. physikal. Ges.*, 1913, **15**, 1017—1026; *Physikal. Zeitsch.*, 1913, **14**, 1172—1175. Compare A., 1912, ii, 738, 1141).—A modified form of van der Waals' equation is put forward, in which association is taken into account. The evaluation of the constants in the critical condition indicates that all normal substances are associated to the extent of 40% at the critical point. A new form of reduced equation is also given, and it is claimed that various facts, which are quite inconsistent with the van der Waals' equation, can be satisfactorily accounted for in terms of the new equation. The ratio of the critical density to that calculated from the simple gas laws, the temperature-coefficient of the vapour pressure at the critical point, the latent heat of vaporisation and the limiting volume of the liquid at absolute zero or under infinite pressure are all in accord with the values indicated by the author's equation. Furthermore, it is found that the association hypothesis leads to the conclusion that there must be a second critical point limiting the coexistence of the solid and liquid forms of all normal substances. H. M. D.

The Phenomena of Equilibria between Silica and the Alkali Carbonates. PAUL NIGGLI (*J. Amer. Chem. Soc.*, 1913, **35**, 1693—1727 *).—The equilibria existing in systems containing the components M_2O, SiO_2, and CO_2 at temperatures of 900—1000° under a pressure of one atmosphere of carbon dioxide have been determined, M being either K, Na, or Li. The various mixtures investigated were made by mixing known weights of the alkali carbonate and silica.

In the case of mixtures of potassium carbonate and silica, the experiments were carried out at 898°, 956°, and 998°. In all cases

* and *Zeitsch. anorg. Chem.*, 1913, **84**, 229—272.

the loss of carbon dioxide was smaller than would correspond with the ratio $SiO_2 : CO_2$; the smaller the concentration of silica the greater is the proportion of carbon dioxide displaced. When the initial proportions are $K_2O : 2SiO_2$, the silica displaces only half the equivalent amount of carbon dioxide at any of the above three temperatures; with lower proportions of silica the amount of carbon dioxide displaced increases with the temperature. The results point to an equilibrium existing in accordance with the equation: $K_2CO_3 + K_2Si_2O_5 \rightleftharpoons 2K_2SiO_3 + CO_2$. Experiments showed that when potassium carbonate is fused with silica, the first reaction takes place according to the equation: $K_2CO_3 + SiO_2 = K_2SiO_3 + CO_2$. The above equilibrium is then set up.

According to the law of mass action, the expression $[K_2SiO_3]^2/[K_2CO_3][K_2Si_2O_5]$ should give a constant value (K) if the concentration of the carbon dioxide remains constant. The value of K increases, however, with increase in concentration of the silica, but the ratio of the "constants" at 898° and 956° remains constant for the different mixtures.

The compound $K_2Si_2O_5$ was obtained pure by heating a mixture composed of $1K_2CO_3 : 2SiO_2$, and its optical properties ascertained. It melts at $1015° \pm 10°$. Potassium carbonate has m. p. 891°.

Similar results were obtained with mixtures of sodium carbonate and silica, except that all the carbon dioxide was replaced when the original mixture contained 1 mol. Na_2CO_3: 1 mol. SiO_2. With less proportions of silica, the fusion contains ortho- and meta-silicate as well as carbonate, so that the equilibrium is represented by the equation: $Na_2CO_3 + Na_2SiO_3 \rightleftharpoons Na_4SiO_4 + CO_2$. Sodium metasilicate was prepared, and its optical properties investigated.

Experiments with mixtures of lithium carbonate and silica indicated that the equilibrium $2Li_2CO_3 + Li_4SiO_4 \rightleftharpoons Li_8SiO_6 + 2CO_2$ exists, but the results were not very satisfactory. T. S. P.

Binary Eutectics between Diphenylamine, *p*-Nitroanisole, and Urethane. Alexei M. Vasiliev (*J. Russ. Phys. Chem. Soc.* 1913, **45**, 1582—1584).—The author applies Flavitzki's law concerning eutectic alloys (A., 1906, ii, 152; compare A., 1910, ii, 606; 1912, ii, 919) to the results of Puschin and Grebenschtschikov (this vol., ii, 852).

For the eutectic formed by diphenylamine and *p*-nitroanisole, calculation according to Flavitzki's equation gives $q/p = 1{\cdot}0136$, which differs little from 1. Taking the latter value as correct, calculation gives a composition of the eutectic differing by less than 0·2 mol. % from that found experimentally. Similar agreement is found with the eutectic of the system diphenylamine–urethane. In consequence of the equivalent molecular lowering pointed out by Flavitzki, the system containing the third pair of these compounds, *p*-nitroanisole and urethane, should give a eutectic for which $q/p = 1$, or, more accurately, 1·026; the actual value for this ratio is, however, 1·343, which is virtually 4 : 3. This anomalous result the author regards as due to the fact that, whereas the eutectic points in the first two cases were determined directly,

that of the third system was obtained only by extrapolation. Reference to the curves and numbers of Puschin and Grebenschtschikov renders it probable that this eutectic contains a greater proportion of *p*-nitroanisole then corresponds with the composition given by these authors; a change in this direction would tend to bring the value of the above ratio nearer to 1.

T. H. P.

A Bomb, with Stirring Arrangement, for the Measurement of Reaction Velocities in Heterogeneous Systems under High Pressures, and a New, High-pressure, Reducing Valve. LUDWIG STUCKERT and MAX ENDERLI (*Chem. Zeit.*, 1913, **37**, 1288).—A description of the apparatus mentioned in the heading is given.

T. S. P.

Heat Content and Velocity of Reaction. MAX TRAUTZ (*Zeitsch. Elektrochem.*, 1913, **19**, 784—794).—A theoretical paper in which a theory of reaction velocity based on the energy content of the molecules is developed. The author postulates the existence of gaseous isomerides in any gas which are termed respectively the "cold modification" and the "hot modification." To the former type a molecular heat of $3/2R$ is attributed, and to the latter one of $5/2R$. Thus, considering one molecule of an ideal gas, of which the fraction x exists in the "hot modification," and $1-x$ in the "cold modification," and the heat of reaction at $T=0$ is Q_0, then the heat content of the system W is given by the equation: $W=(1-x)3/2RT+x(5/2RT+Q_0)=3/2RT+x(Q_0+RT)$. As a result of the hypcthesis the author gives reasons for doubting the monatomic nature of the rare gases, and even of doubting their elementary uature, mainly on account of the determinations of Scheel and Heuse (this vol., ii, 183), which show that the molecular heat of helium has a positive temperature-coefficient instead of being independent of temperature as a monatomic gas should be.

J. F. S.

Some Physico-chemical Applications of Maxwell-Berthoud's Equation of Re-distribution. GEORGES BAUME (*Compt. rend.*, 1913, **157**, 774—776.* Compare Berthoud, A., 1911, ii, 578).—A theoretical discussion of the factors governing reaction velocities as deduced from Berthoud's modification of Maxwell's equation. When the velocity of reaction is measurable, the number of active molecules is small, and the mean temperature of the system is sensibly different from that of the molecules, from which it results that: (1) The increase in the number of active molecules with rise in temperature increases with the molecular heat at constant volume C_v. (2) The velocity of reaction is, in general, doubled or tripled for a rise of 10° in temperature, this increase being greater as C_v is greater. (3) The active molecules have a velocity much nearer to the mean square velocity, the greater is C_v. (4) It is possible to state the process of chemical reactions according to the value of C_v. (5) Addition molecules can only be formed from molecules with low velocities.

W. G.

* and *Arch. Sci. phys. nat.*, 1913, [iv], **36**, 439—442.

Photochemical Kinetics of Hydrogen and Chlorine Combination. MAX BODENSTEIN and WALTER DUX (*Zeitsch. Elektrochem.*, 1913, **19**, 836—856; *Zeitsch. physikal. Chem.*, 1913, **85**, 297—328).—An apparatus is described by means of which the velocity of combination of hydrogen and chlorine in light of measured intensity has been measured. The hydrogen and chlorine are admitted and their pressures determined by means of a quartz glass manometer. Then the light is allowed to act for a stated time, and the amouut of hydrogen uncombined is measured by freezing the chlorine and hydrogen chloride by cooling with liquid air, the pressure of the residual hydrogen then being determined. In this way it is shown that with a given light intensity, the velocity of the reaction is proportional to the square of the chlorine concentration, inversely proportional to the concentration of the oxygen which may be present, and independent of the concentration of the hydrogen chloride, water vapour, and hydrogen. In the case of the hydrogen this is only true so long as the concentration is not less than one-quarter that of the chlorine. The author then develops theoretically a scheme of the mechanism of photochemical reactions. The reactions are divided into two groups: (1) Primary; (2) Secondary. It is assumed that the absorption of light energy ionises the atoms into an electron and a positively charged residue. The reactions occurring between the positively charged residues and other molecules constitute primary reactions, and of these four characteristics are specified: (1) A proportionality exists between the amount of reaction and the absorbed light energy, and consequently a velocity equation is possible. (2) The reaction is independent of the concentration and nature of the impurities. (3) They are independent of the temperature; and (4) each molecule taking part in the change uses one quantum or a very small number of quanta of energy. The secondary reactions are those brought about by the free electrons attaching themselves to neutral molecules, and thereby inducing a reaction. The kinetics of the secondary reactions are developed mathematically, treating the electron as a chemical molecule. In this way it is shown that 10^6 chlorine atoms are caused to combine, while one positive chlorine residue combines. The author considers a large number of photochemical reactions which have been previously published. These he divides into primary and secondary processes, and shows that they can all be explained without further hypothesis on the present basis. It is further shown that reactions brought by electric discharge through gases or by radioactive radiations can be brought readily under the same scheme. J. F. S.

The Combustion of Gaseous Mixtures. J. TAFFANEL and LE FLOCH (*Compt. rend.*, 1913, **157**, 595—597. Compare this vol., ii, 574).—The authors have measured the rate of combustion of various mixtures of methane and air at temperatures inferior to their ignition points, and by use of formulæ havo extrapolated their results to determine the ignition temperatures of these mixtures, the calculated results agreeing closely with those already found.

They have further calculated the temperatures of combustion of mixtures containing from 3 to 6% of methane, and find that in all cases it is in the neighbourhood of 1310°. W. G.

The Combustion of Gaseous Mixtures and the Velocities of Reaction. J. TAFFANEL (*Compt. rend.*, 1913, **157**, 714—717).—A theoretical and mathematical discussion of results already published (compare Taffanel and Le Floch, this vol., ii, 574). W. G.

The Extinction of Flames. WILLEM P. JORISSEN (*Chem. Weekblad*, 1913, **10**, 961—962).—A criticism of the results obtained by Harger ("Coal, and the Prevention of Explosions and Fires in Mines") in investigations of the limits of explosion of paraffins, acetylene, and coal-gas. A. J. W.

Velocity of the Reaction between Sulphuric Acid and Acetone. ROBERT KREMANN and HERBERT HÖNEL (*Monatsh.*, 1913, **34**, 1469—1487).—Since no variation in titration values occurred when acetone and anhydrous sulphuric acid were mixed at 0°, even after some hours, the possibility of the formation of a monobasic mesitylsulphuric acid was negatived. The action of sulphuric acid on acetone is therefore entirely that of the elimination of water, but it was required to know whether the acid acted dynamically and became hydrated, or as a catalyst.

The reaction was studied by measuring the conductivity of sulphuric acid in excess of acetone at 0°, immediately after mixing, and at different intervals. Assuming that the dielectric constant of mesityl oxide is about the same as acetone, that is, much less than that of water, and that the concentration of acetone remains practically constant, it follows that the increase of conductivity is proportional to the amount of water formed. In the first place, the initial conductivity of sulphuric acid in various mixtures of water and acetone was measured. Anhydrous acid was dropped into the mixture in a freezing-bath, and then placed in an ice thermostat, when the conductivity was determined, and finally the concentration of acid was obtained by titration. One series of curves shows the relation between the conductivity and the concentration of acid in pure and in each diluted acetone. From these, another series was obtained, which shows the relation between conductivity and water-content for such concentrations of acid as were chosen for the further kinetic experiments. In the case of moderate concentrations of acid (up to $0.5N$), the conductivity rises quickly at first with the water concentration. From 1 to 3 grams of water per 100 c.c., however, the conductivity remains almost constant, after which it rises again. This is, no doubt, due to the formation of a hydrate taking pre-eminence in this region.

The conductivity of different mixtures of sulphuric acid and acetone was then measured at different intervals, and from the above curves the amount of water formed was obtained. Curves connecting this quantity with time, for each concentration of acid, are given. They show that the speed of the reaction rises with

the concentration, and that the equilibrium point is also dependent on the concentration of acid. This indicates that the reaction is not catalytic, but follows the course:

$$2\text{Acetone} + H_2SO_4 \longrightarrow H_2SO_4,H_2O + \text{Mesityl oxide}.$$

The amount of water formed in a short time (fifteen minutes) in a normal solution of sulphuric acid in acetone, at 0°, is practically negligible.

J. C. W.

Neutral Salt Action on the Change Acetochloroanilide ⟶ p-Chloroacetanilide in the Presence of Hydrochloric Acid. ALBERT C. D. RIVETT (*Zeitsch. physikal. Chem.*, 1913, **85**, 113—128. Compare this vol., ii, 202).—The reaction constants of the change acetochloroanilide ⟶ *p*-chloroacetanilide in the presence of hydrochloric acid have been measured in solutions to which chlorides of the metals lithium, sodium, potassium, rubidium, cæsium, ammonium, magnesium, calcium, barium, strontium, and zinc have been added. The experiments were carried out at a number of concentrations, and a series of measurements was also made in the presence of sulphuric acid. It is shown that the velocity constant k can be obtained by means of the formula:

$$k = [HCl]\{0{\cdot}050 + a[H^{\cdot}] + b[Cl'] + d[M^{\cdot}]\},$$

where a, b, and d are specific constants depending on the nature of the ions. It is shown that change of temperature is without effect in the cases examined. Ammonium chloride behaves abnormally; this is explained on the basis of the theory of Orton and Jones (T., 1909, **45**, 114). The relationship between the concentration of the hydrochloric acid and the velocity of the reaction is discussed.

J. F. S.

The Retarding Action of Small Quantities of Water on the Decomposition of Diazoacetic Esters in Alcoholic Solution. I. W. S. MILLAR (*Zeitsch. physikal. Chem.*, 1913, **85**, 129—169).—The velocity of the decomposition of diazoacetic ester by picric acid in ethyl, methyl, and *iso*butyl alcohol solutions has been determined. The influence of the addition of small quantities of water to the alcoholic solutions retards the reaction in a very marked degree, the action being greatest in *iso*butyl alcohol, and least in methyl alcohol. On increasing the concentration of the water, the velocity sinks until a minimum value is reached, which in the case of methyl alcohol occurs at a concentration of 10 mols. of water per litre of mixture, and with ethyl alcohol at 6 mols. per litre. The constants calculated for the reaction on the unimolecular basis slowly decrease, and this is shown by electrical conductivity measurements to be due to a reaction between the picric acid and the solvent. It is also shown that there is a proportionality between the velocity of the reaction and the electrical conductivity in these cases. It is shown that up to a water concentration of 0·6% in ethyl alcohol the reaction is unimolecular, but at this point the water as well as the alcohol react with the diazo-ester. The hydrogen ion alcoholate is assumed, as in the case of esterification (Goldschmidt, A., 1912, ii, 1154), and the hydrolytic constant v is calculated.

This is found to be 0·57 for methyl alcohol; 0·26, ethyl alcohol; and 0·12 for *iso*butyl alcohol. In the case of ethyl alcohol, taking account of the change in the ionisation of picric acid by the addition of water, it is found to be 0·15. J. F. S.

The Retarding Action of Small Quantities of Water on the Decomposition of Diazoacetic Esters in Alcoholic Solution II. HERMANN BRAUNE (*Zeitsch. physikal. Chem.*, 1913, 85, 170—210. Compare preceding abstract).—The velocity of the decomposition of the methyl and ethyl diazoacetic esters in ethyl alcohol by trichloroacetic acid, 2 : 4 : 6-trinitrobenzoic acid, sulphosalicylic acid, and trichlorobutyric acid has been determined at 25°. The influence of the addition of small, measured quantities of water on the reaction constant has also been studied. It is shown that the addition of water retards the reaction, and to about the same extent in every case if the change in the ionisation of the catalysing acid is considered. Up to a water concentration of 0·3 mol. per litre the results for the catalysis agree with the values calculated from Goldschmidt's formula: $k(r+n)=C$ (A., 1912, ii, 1154). According to Goldschmidt's theory, the dimensions of r should be the same for all acids and substances catalysed by those acids, and this condition is fulfilled in the case of the acids used in the present investigation, although the value of r for trichlorobutyric acid is somewhat larger than in the other cases. The reaction is shown not to be a simple hydrogen ion catalysis, for the velocity constant increases more rapidly than the concentration of the hydrogen ion. The amount of divergence from strict proportionality between the reaction constant and the hydrogen concentration is different in every case, and appears to be specific for each acid. The divergence is supposed to be due to the presence of side reactions, and an attempt is made to substantiate the assumption by means of reactions in the presence of neutral salts. Reactions were therefore carried out in the presence of aniline trichloroacetate, the results of which confirm the above assumption, and also confirm the analogy between the diazo-ester catalysis and the catalytic esterification as explained by Goldschmidt. It is also shown that the reaction between the diazo-ester and the catalysing acid is retarded by water. J. F. S.

The Influence of Alcohol and of Sucrose on the Rate of Solution of Cadmium in Dissolved Iodine. RALPH G. VAN NAME and D. U. HILL (*Amer. J. Sci.*, 1913, [iv], 36, 543—554).—The effect of various concentrations of ethyl alcohol (0·25—3 molar) and of sucrose (1/32—1 molar) on the rate of solution of cadmium in an iodine–potassium iodide solution has been measured at 25°. Since in such processes of dissolution in purely aqueous solutions it has been shown that the rate of diffusion at the metal surface is the determining factor (A., 1911, ii, 973), it follows, assuming that the thickness of the diffusion layer is not affected by the concentration of the non-electrolyte, that the results in aqueous solutions containing non-electrolytes

should be in accordance with Arrhenius's equation for the effect of non-electrolytes upon the rate of diffusion of electrolytes, namely, $D = D_0(1 - ma/2)^2$, where D_0 and D are respectively the diffusion coefficients of the electrolyte in solution in pure water, and after the addition of the electrolyte, m is the molar concentration of the non-electrolyte, and a is a constant. The effect of the non-electrolyte on the reaction velocity above-mentioned should be in accordance with this equation, substituting the velocity constants for D_0 and D.

With alcohol, the observed velocity constants agree well with the constants calculated from Arrhenius's equation if an arbitrary, although, so far as can be judged by analogy, not impossible, value is chosen for the constant a. With sucrose no value of a gives a good agreement.

In both cases, but especially in that of sugar, the diminution of the reaction velocity appears to be larger than would be expected from the available diffusion data.

The probable effect of an increase in viscosity in increasing the thickness of the diffusion layer is discussed, and is suggested as a possible explanation of the discrepancies. T. S. P.

The Influence of Foreign Substances on the Activity of Catalysts. II. Experiments with Palladium as Hydrogen Carrier. CARL PAAL and ARTHUR KARL (*Ber.*, 1913, **46**, 3069—3076).
—In a previous communication (A., 1911, ii, 479), the authors have investigated the behaviour of palladium as hydrogen carrier in the presence of metals, and have found that only magnesium, nickel, and cobalt are without influence on the catalytic effect of the palladium, whilst aluminium, iron, copper, zinc, tin, silver, or lead behave as anti-catalysts. The present paper deals with the action of compounds of these elements.

The compounds were coated with palladium by treating them with a faintly acid solution of palladium chloride, whereby a thin film of palladium hydroxide is formed. After washing and drying, the products were moistened with ether, and the palladium hydroxide reduced by hydrogen at the ordinary temperature. Their action as hydrogen carriers in the reduction of liquid unsaturated esters was investigated in the apparatus described by Paal and Gerum (A., 1908, ii, 392).

The authors are led to the conclusion that those metals which have an anti-catalytic influence on palladium show a similar action when used in the form of their oxides, hydroxides, or carbonates. This is most distinctly shown by palladianised basic lead carbonate, which, like the metal, absolutely destroys the catalytic activity of palladium in all circumstances. Palladianised cadmium carbonate, zinc oxide, zinc carbonate, ferric hydroxide, and aluminium hydroxide, like the palladianised metals, are either incapable or only slightly capable of acting as hydrogen carriers to unsaturated organic compounds at the ordinary pressure, whilst, at higher pressures and temperatures, they cause a slight hydrogenation. On the other hand, magnesium oxide, like magnesium itself, does not

inhibit the catalytic action of the palladium; hydrogenation even appears to proceed more rapidly in the presence of the oxide than of the metal, doubtless due to the larger surface exposed. H. W.

The Influence of Neutral Salts on Catalytic Reactions in Various Solvents. H. C. S. SNETHLAGE (*Zeitsch. physikal. Chem.*, 1913, **85**, 211—262).—The influence of the addition of picrates of *p*-toluidine, tripropylamine, β-naphthylamine, carbamide, *o*-aminobenzoic acid, acetoxime, acetamide, *p*-nitroaniline, acetanilide, o-nitroaniline, and propionitrile has been determined for the decomposition of diazoacetic ester in absolute alcohol in the presence of picric acid. It is shown that the catalytic action of picric acid is reduced by the addition of picrates, and that the value of the velocity constant converges to a value which is different from zero. This is attributed to the catalytic action of the undissociated acid. A formula of hyperbolic nature is deduced, by means of which the velocity constant can be calculated from the concentration of the added salt. This formula has the form $k=\{\gamma . k_H + (1-\gamma)k_M\}C$, in which C is the concentration of the salt in equivalents per litre, k_H the velocity constant in a solution containing one equivalent of hydrogen ions, k_M the velocity constant for a solution containing one equivalent of undissociated acid, and γ the degree of dissociation. The formula holds for $0{\cdot}00909N$-picric acid and the three salts, *p*-toluidine picrate, tripropylamine picrate, and β-naphthylamine picrate. The above-mentioned three picrates retard the reaction by the same amount when present in the same concentration, and when present in the absence of free acid have no catalytic action. The other bases mentioned above, when added to an equivalent quantity of picric acid, also decrease the velocity constant of $0{\cdot}00909N$-picric acid decomposition, but to a much smaller extent, which is different in the different cases. This points to an "alcoholysis" of the picrates. In the case of carbamide picrate, it is shown in one case that the velocity constant increases proportionally to the square-root of the salt concentration. A formula is deduced by means of which the value of k_M can be calculated, and it is shown that the calculated and observed values of k_M agree satisfactorily. The velocity constant of the acid catalysed reaction can be calculated if the value of γ (determined from electro-conductivity), k_M and k_H are known. The velocity constant in the calculation is regarded as the sum of two factors, one proportional to the hydrogen ion concentration, and the other proportional to the undissociated acid. The values of k_M and k_H are calculated for a number of reactions in ethyl alcohol, methyl alcohol, and water from previously published work of the author (A., 1912, ii, 749), Goldschmidt (A., 1912, ii, 1154), and others. In the cases examined it is shown that the ratio k_M/k_H is larger for acids with a large affinity constant, and smaller for those with a small affinity constant. If reactions of the same type occur in a stated solvent and are catalysed by the same acid, then the value k_M/k_H is constant even when the absolute values of k_M and k_H are very different. When the acid is used to catalyse reactions of

different types the ratio k_M/k_H is in most cases practically identical for both reactions. There is obviously a close relationship between k_M/k_H and the affinity constant of the acid, which is but little influenced by the solvent. The value of k_M/k_H for the strongest acids is approximately unity in ethyl alcohol and methyl alcohol solutions, so that in these solutions the velocity constant is approximately proportional to the total concentration of the acid (dissociated + undissociated). The strong acids in water solution have a value greater than unity, and this offers a possible explanation for the increase in the velocity of the inversion of sucrose on the addition of neutral salts. J. F. S.

In Commemoration of the Centennial of the Publication of the Berzelian System of Symbols. HENRY LEFFMANN (*J. Amer. Chem. Soc.*, 1913, **35**, 1664—1666).—A translation of Berzelius' original paper on "The chemical signs and the method of employing them to express chemical proportions." T. S. P.

Constitution and Structure of the Chemical Elements. HAWKSWORTH COLLINS (*Chem. News*, 1913, **108**, 235—236).—The author claims to have anticipated certain recent observations relating to the connexion between the different elements. In reference to elements of atomic weight less than 60, it is pointed out that the valency of an element is even or odd according to whether its atomic weight approximates or is nearer to an even or odd whole number. Nitrogen is regarded as a possible exception. H. M. D.

Theory of a Nuclear Homology in the Periodic System. DAN RADULESCU (*Chem. Zentr.*, 1913, ii, 922; from *Bull. Soc. Stiinte, București*, 1913, **20**, 500—513).—The author puts forward views relating to the constitution of the atoms and the interpretation of the periodic system. It is supposed that every element of higher atomic weight consists of two parts, which are distinguished as the "characteristic function" and the "homology nucleus." The "characteristic functions" of the heavier elements are closely related in mass and properties to those of the typical elements hydrogen, helium, oxygen, carbon, nitrogen. In accordance with this, values are assigned to the "proto-elements," from which the characteristic functions are derived, which represent sub-multiples of the atomic weights of the typical elements. The homology results from the successive addition of certain structural nuclear elements which are regarded as derived from hydrogen and helium. H. M. D.

Constitution of Atoms and Molecules. III. N. BOHR (*Phil. Mag.*, 1913, [vi], **26**, 857—875. Compare this vol., ii, 689, 943).—The author's theory relative to atomic structure is further developed and applied to molecules. The idea that the atoms are formed by successive binding of a number of electrons cannot be utilised in considering the formation of a system containing more than a

single nucleus, for in the latter case there is nothing to keep the positively charged nuclei together during the binding process. It must therefore be assumed that molecules are formed by the interaction of systems, each containing a single nucleus, which have already bound a number of electrons.

The simple case of a system consisting of two nuclei and of a ring of electrons rotating round the line connecting them is discussed in detail with special reference to the constitution of the hydrogen molecule, and a simple method of procedure is indicated by which it is possible to follow, step by step, the combination of two atoms to form a molecule. The views put forward lead to the conclusion that the breaking up of a hydrogen molecule in consequence of the slow separation of the nuclei will result in the production of two neutral atoms, and not of a positively and a negatively charged atom. This is in agreement with deductions drawn from observations on the behaviour of positive rays.

Indications are also given of the configurations to be expected for systems containing a greater number of electrons, and the paper concludes with an explicit statement of the assumptions which are made in connexion with the author's theory. H. M. D.

A New Mechanical Agitator for Laboratory Use. VICTOR GRIGNARD (*Bull. Soc. chim.*, 1913, [iv], **13**, 952—955).—The apparatus is designed for use in cases where a reagent is to be added with constant agitation, and where it may be necessary to use a reflux condenser. It consists of a circular plate of iron or copper, 30 cm. in diameter, and pierced with three holes 10 cm. in diameter, in which flasks can stand. The plate is covered with asbestos board, and can rotate about its vertical axis on a pivot fixed to the base of a heavy retort stand. The plate is put in motion by a crank connected to the periphery of the plate, and actuated from a small water motor. If a flask with a reflux condenser and a supply tube is to be used, the two latter are connected to the flask by a T-piece and supported loosely in a ring attached to the rod of the retort stand. The plate is provided with clips in which closed bottles can be held for agitation. The apparatus is figured in the original. T. A. H.

A Microfiltration Method by Centrifugal Force. CASIMIR STRZYZOWSKI (*Österr. Chem. Zeit.*, 1913, [2], **16**, 123—124).—A sketch, with description of an apparatus employed for filtering minute quantities of liquids by suction or centrifugal force. F. M. G. M.

A New Form of Condenser. PIETER J. MONTAGNE (*Chem. Weekblad*, 1913, **10**, 960—961).—A modification of the ordinary form of condenser, both ends of the inner tube being bent so that they are vertical when the condenser is clamped at an angle of 30° to the horizontal. By attaching a flask to the lower end a reflux condenser is obtained; by transferring it to the other end, an ordinary distillation can be effected. A. J. W.

Extraction Apparatus. MAURICE FRANÇOIS (*J. Pharm. Chim.* 1913, [vii], **8**, 409—410 *).—The apparatus consists of a wide tube provided with a stem which is attached to the flask holding the solvent; the top of the tube is connected with a reflux apparatus. A separate, narrow tube is placed down the centre of the wide tube; the lower end of this narrow tube is expanded slightly, and fits over the upper end of the stem, whilst the top is closed by a conical bulb having a small hole at its lower edge. A small layer of cotton-wool is packed round the base of the narrow tube, the material to bo extracted is placed above this layer, and in the space between the narrow tube and the wall of the wide tube, and covered with a second layer of cotton-wool. The vapours of the solvent pass from the flask up the narrow tube into the condenser, and the condensed liquid falls thence on to the material and returns to the flask. W. P. S.

Inorganic Chemistry.

Triatomic Hydrogen Molecules. JOHANNES STARK (*Zeitsch. Elektrochem.*, 1913, **19**, 862—863).—A theoretical paper in which the constitution of the triatomic hydrogen molecule is discussed on the basis of Stark's valency hypothesis. A method is proposed for obtaining triatomic hydrogen with the object of examining it chemically (compare also Stark, this vol., ii, 901; Thomson, A., 1912, ii, 885; this vol., ii, 502, 820). J. F. S.

Displacement of Acids by Hydrogen Peroxide. JOACHIM SPERBER (*Chem. Zentr.*, 1913, ii, 1195—1196; from *Schweiz. Woch Chem. Pharm*, 1913, **51**, 469—472).—If solutions of potassium ferrocyanide or ferricyanide are evaporated in presence of hydrogen peroxide, the corresponding acids are set free. Hydrogen sulphide is liberated readily from the alkali metal sulphides, and also, although less readily, from the alkaline earth metal sulphides. Ammonium hydrogen sulphide gives rise to hydrogen sulphide and traces of ammonia, but oxygen is not set free. If polysulphides are present, sulphur is deposited. H. M. D.

Fluorine is a Constant Element in the Emanations from the Earth's Centre. ARMAND GAUTIER (*Compt. rend.*, 1913, **157**, 820—825).—In support of his view that fluorine is to be found in all rocks, thermal waters, and vapours coming from the earth's core, the author has examined the vapour obtained from fumerole fissures in the crater of Vesuvius, and also hot water obtained from a sounding hole 150—170 metres deep at Larderello, in Tuscany. In the gas from Vesuvius he found 0·110 mg. of fluorine per litre measured at 760 mm., whilst in the condensed water from

* and *Anal. Falsif.*, 1913, **6**, 608—609.

the boric acid containing vapours of Tuscany he found 3·72 mg. per litre, a value closely in accord with the fluorine content of the mineral waters from Vichy and Luxeuil. W. G.

New Method of Preparing Colloidal Sulphur and Selenium. JULIUS MEYER (*Ber.*, 1913, **46**, 3089—3091. Compare Jannek, this vol., ii, 948).—Sulphur and selenium are readily soluble in concentrated hydrazine hydrate, forming viscous, deeply coloured solutions. In this case, definite chemical change occurs, probably in accordance with the equations:

$$3NH_2\cdot NH_3\cdot OH + 3S = 2H_2N\cdot NH_3\cdot SH + H_2N\cdot NH_3\cdot SO_3H, \text{ or}$$

$$6NH_2\cdot NH_3\cdot OH + 3S = 2(H_2N\cdot NH_3)_2S + (H_2N\cdot NH_3)_2SO_3 + 3H_2O.$$

If the solution of selenium is cautiously acidified after a few days, the odour of hydrogen selenide is very obvious, whilst Lobry de Bruyn (A., 1895, ii, 496) has shown that the similar solution of sulphur smells of hydrogen sulphide.

The selenium solution, when largely diluted, gives an intensely red solution, which is extraordinarily stable; it may be preserved unchanged for months, and is unaltered by prolonged boiling. On preservation, minute quantities of red selenium separate, which, however, disappear when the solution is agitated. The sulphur solution, when similarly treated, yields immediately a clear, lemon-yellow solution, which becomes yellowish-white owing to the formation of colloidal sulphur. In the concentrated condition, the sulphur solution is not so stable as the selenium solution. The solutions cannot be dialysed. H. W.

Crystallised Sulphuric Acid, H_2SO_4,H_2O. A. D. DONK (*Chem. Weekblad*, 1913, **10**, 956—957).—When cooled with ice, a mixture of 84—85% sulphuric acid with a large excess of sulphate of lead or barium deposits crystals of the monohydrate, H_2SO_4,H_2O. A. J. W.

Crystallised Sulphuric Acid and its Hydrate. WILLEM P. JORISSEN (*Chem. Weekblad*, 1913, **10**, 962—963. Compare preceding abstract).—A rapid crystallisation of the monohydrate of sulphuric acid is induced by cooling 83·3—84% sulphuric acid with ice. A. J. W.

New Determination of the Atomic Weight of Selenium. JULIUS MEYER (*Zeitsch. Elektrochem.*, 1913, **19**, 833—835).—Selenium is quantitatively oxidised in a quartz bulb by passing a stream of nitrogen peroxide and oxygen over it at 215°. The last traces of nitrogen peroxide are removed by distilling the selenium dioxide repeatedly in the same bulb. A mean of five experiments gives the value for selenium: Se = 79·135. As a control of the method the selenium dioxide was reduced by hydrazine hydrate, and it was found that the quantity of selenium used in an experiment could be entirely regained from the reduction experiment. Incidentally it is shown that both crystalline and amorphous selenium are soluble to a considerable extent in concentrated hydrazine hydrate solution.

producing thereby stable selenium sols, which are easily precipitated by hydrochloric acid. A series of vapour pressures of selenium dioxide and selenious acid at temperatures 20—320° are given, thus showing that the conversion of selenious acid into selenium dioxide by heat is not suitable for the determination of the atomic weight of the element. J. F. S.

Hydrogen Selenide and Hydrogen Telluride as Acids. LUDWIK BRUNER (*Zeitsch. Elektrochem.*, 1913, **19**, 861).—A decinormal solution of hydrogen selenide under atmospheric pressure is dissociated to the extent of 4·1%, and has an affinity constant of $1{\cdot}7\times10^{-4}$. A solution of hydrogen telluride 0·01N, in the absence of air, has a specific conductivity of 2×10^{-3}, and at this concentration is 50% dissociated. If a bubble of oxygen is allowed to enter the conductivity-vessel, the hydrogen telluride is at once decomposed with the deposition of tellurium, and the conductivity at once falls to almost zero, proof that the original conductivity is due to the hydrogen telluride. From these experiments it is shown that the elements of the fifth group of the periodic system increase in their acidic character with increase in the atomic weight. This is shown by the series H_2O, H_2S, H_2Se, H_2Te.
J. F. S.

The Oxidation of Nitrogen in the Electric Discharge. ADOLF KOENIG and E. ELÖD (*Ber.*, 1913, **46**, 2998—3009).—The reply of Fischer and Hene (this vol., ii, 317) to the criticism by König (this vol., ii, 210) of their interpretation of their results on the combination of nitrogen and oxygen (this vol., ii, 132) is stated to be unconvincing.

The authors have made experiments similar to those of Fischer and Hene, with a spark discharge between iron electrodes, but with a somewhat larger chamber constructed of glass for the discharge. Their results indicate that in spite of special precautions to prevent the second gas diffusing back into the one which is being submitted to the discharge, such diffusion does occur, probably aided by inevitable eddies in the chamber. In a check experiment in which nitrogen was submitted to the discharge, and then, passing into the exit-tube from the chamber, was mixed with an entering stream of methane, the spectrum of the discharge soon showed the presence of cyanogen in the chamber, and the collected gases contained hydrogen cyanide.

The view is still held that in the combination of nitrogen and oxygen under the influence of the electric discharge, probably both the reacting gases become activated before combination ensues.
D. F. T.

Oxidation of Nitrogen and Oxygen. WILLIAM W. STRONG (*Amer. Chem. J.*, 1913, **50**, 204—212).—Strutt (A., 1911, ii, 482; 1912, ii, 126) and Strutt and Fowler (A., 1911, ii, 678; 1912, ii, 214) have investigated reactions in which nitrogen is involved. The method consists in producing modifications of various sub-

stances in the electrical discharge and studying the spectra of the after-glows. The after-glow in air is regarded as probably due to the oxidation of nitric oxide by ozone.

It has been considered probable that the electrical method may be of service in elucidating the mechanism of formation of ozone and nitric oxide, and the author has therefore carried out some preliminary experiments with the corona discharge, this method enabling the ionic streams to be partly controlled.

E. G.

Flames Containing Nitric Oxide. ALFRED REIS and OLGA WALDBAUER (*Zeitsch. physikal. Chem.*, 1913, **85**, 62—98).—Steadily burning flames have been produced from a mixture of the gases methane, oxygen, and nitric oxide. These flames could be separated into their two cones, which burnt quietly even when the proportions of the gases were varied over wide limits. It is shown in the case of flames containing small percentages of nitric oxide, that the gases coming from the inner cone contain ammonia, acetylene, and hydrogen cyanide. An examination of the composition of the gases between the two zones at different heights above the inner cone shows that the hydrogen cyanide decreases with increasing height, whilst the ammonia rises to a maximum and then falls, thus showing that the ammonia is formed from the hydrogen cyanide. In the case of mixtures containing a high percentage of nitric oxide, the inner cone shows the characteristic appearance of substances burning in nitrogen peroxide. The temperature, light emission, and velocity of explosion of this inner cone are investigated. It is shown that in the combustion in this inner cone 90% of the nitrogen peroxide is transformed into nitric oxide, which then passes out of the inner cone unchanged; about 33%—25% of the methane also escapes from the inner cone unburnt. The hydrogen is almost completely oxidised, but the carbon monoxide is only oxidised to a very small extent. Measurable quantities of formaldehyde are to be found in the gases between the two zones. The gaseous mixture between the zones consists of about 40% of nitric oxide with combustible gases and water vapour. Analysis of the gases between the zones at various heights shows that the nitric oxide is slightly decomposed, but that the methane is unchanged: the concentration of hydrogen increases whilst that of the carbon monoxide falls. When the gases between the two zones contain sufficient oxygen, a new cone appears between the inner and outer cones; this is termed the middle cone, and in it the combustible gases are burnt at the expense of the nitric oxide.

J. F. S.

Explosion of Nitrogen Iodide Under the Influence of Acoustic Waves. ERNST BECKMANN and OTTO FAUST (*Ber.*, 1913, **46**, 3167—3168).—Champion and Pellet (this Journ., 1872, 871: 1873, 31) claim to have exploded nitrogen iodide by means of acoustic waves. It is now shown that nitrogen iodide cannot be detonated even with a wide range of acoustic vibrations.

E. F. A.

Ammonium Peroxides. JOHANNES D'ANS and O. WEDIG (*Ber.*, 1913, **46**, 3075—3076. Compare Melikov and Pissarjevski, A., 1898, ii, 161, 219, 292).—When dry ammonia is passed into a solution of pure hydrogen peroxide in absolute ether which is cooled to about −10°, crystals of ammonium hydroperoxide, NH_4O_2H, separate, which, in the presence of a further quantity of ammonia, disappear with the formation of an oily layer. The latter solidifies with some difficulty at about −40°, and yields *ammonium peroxide*, $(NH_4)_2O_2$, which commences to decompose with evolution of gas at −10°, and has m. p. about −2°. It readily loses ammonia, forming ammonium hydroperoxide if the temperature is not allowed to rise too high.

Ammonium hydroperoxide has m. p. about +14° (decomp.) instead of −20° as given by Melikov and Pissarjevski. H. W.

Modifications of Phosphorus. ALFRED STOCK and ERICH STAMM (*Ber.*, 1913, **46**, 3497—3513).—Hittorf's phosphorus, prepared according to the method of Stock and Gomolka (A., 1910, ii, 30), does not conduct electricity, and there are no sufficient reasons for calling it "metallic phosphorus." In the purification, the lead dioxide produced during electrolysis should be removed by levigation before the treatment with hydrochloric acid. Hittorf's phosphorus is volatile at 280°, whereas only traces of red phosphorus volatilise at that temperature.

In contradiction to Smits and Leeuw (A., 1911, ii, 263), it is found that the melting point of colourless phosphorus is not altered by heating it to 100°, followed by rapid cooling.

Red phosphorus, formed by heating pure, colourless phosphorus at 300°, may be made to melt at temperatures varying from 579° to 601°. The various phenomena observed indicate that the melting point is affected by displaceable equilibria which exist between different modifications of phosphorus; it is, for example, possible to maintain a dark modification in contact with a clear fusion for hours together at about 545°.

In contradistinction to the statements of Arctowski (A., 1896, ii, 559), red phosphorus is not appreciably volatile at 100°, or even at 200°. The vapour from red phosphorus heated at 280—400° condenses partly as red phosphorus. Hittorf's phosphorus at 300—350° gives a vapour which condenses as colourless phosphorus, even when the vapour is subjected to intermediate heating at 500°. Colourless phosphorus also gives a colourless distillate; it follows that the vapour of red phosphorus must contain molecules of the red modification, which is in accordance with the fact that under appropriate conditions red phosphorus can be sublimed in the crystalline form (Stock, Schrader, and Stamm, A., 1912, ii, 639).

Attempts were made to see if there was a relation between the dissociation of phosphorus vapour, and the amount of red phosphorus formed when the vapour is quickly condensed, since it has previously been shown (Stock, Schrader, and Stamm, *loc. cit.*) that the polymerisation of P_2 to P_4 molecules is a slow process. The

vapour was heated in a tube at 900°, and then carried, by a stream of nitrogen, into a cold part of the tube, where it condensed partly as red and partly as colourless phosphorus. The latter could then be separated by distillation at 200—250°, and the relative amounts of the two forms determined by weighing. The results were not concordant, but nevertheless indicated that more red phosphorus is formed than corresponds with the dissociation into P_2-molecules, that is, that the P_4-molecules also take part in the formation of red phosphorus, possibly in accordance with the equation: $xP_2+yP_4=P_{(2x+4y)}$. That P_2-molecules take part in the formation of red phosphorus cannot be doubted, since phosphorus vapour heated at 1200° under 5 mm. pressure gives a deposit of red phosphorus which does not contain more than 1% of colourless phosphorus.

The proportion of red phosphorus formed from phosphorus vapour at 300° was determined. Colourless phosphorus was distilled into narrow, short tubes, in such quantity that it was completely vaporised at the temperature of the experiment. On prolonged heating red phosphorus deposited on the walls of the tube, even if the tubes had been heated previously to 1000°, in order to destroy all nuclei of red phosphorus. The results were affected by the fact that the surface of the tubes had a catalytic effect on the formation of red phosphorus, but comparative experiments showed that the quantity of red phosphorus formed diminishes as the pressure decreases; below pressures of about half-an-atmosphere, no red phosphorus is produced.

When the tubes contained so much colourless phosphorus that it did not all vaporise at 300°, the liquid remaining rapidly changed into loose, red phosphorus, which then became more compact, by reason of red phosphorus depositing from the vapour into the pores. This explains the "cementation" of phosphorus first observed by Lemoine in 1871.

The authors discuss the above and other results from the point of view that the following two equilibria exist: $P_4 \rightleftarrows 2P_2$ and $xP_2+yP_4 \rightleftarrows P_{(2x+4y)}$, assuming, in accordance with the experimental evidence, that the polymerisation of P_2 to P_4-molecules takes place relatively slowly, whilst the formation of red phosphorus $[P_{(2x+4y)}]$ takes place rapidly.

T. S. P.

Vaporisation of Phosphorus in Oxygen and Other Gases. MIECZYSLAW CENTNERSZWER (*Zeitsch. physikal. Chem.*, 1913, 85, 99—112).—It is shown that phosphorus volatilises in pure oxygen without oxidation in just the same way as it does in other gases, and thus obeys Dalton's law of partial pressures. The vapour pressure of phosphorus in oxygen, hydrogen, carbon dioxide, and coal-gas has been determined at low temperatures. The method consists in leading the dry pure gases in measured quantities slowly over three porcelain boats containing sticks of specially purified phosphorus. Similar experiments were made in air, in which a little iodobenzene vapour was contained. The following values were obtained: oxygen at 20°, $p=0.0251$ mm. mercury; hydrogen

at 20°, p=0·0253 mm.; 25°, p=0·0426 mm.; 30°, p=0·0724 mm.; 35°, p=0·0889 mm.; 40°, p=0·1221 mm.; carbon dioxide at 20°, p=0·0312 mm.; coal gas at 20°, p=0·0242; and in air at 20°, p=0·0253. It is shown that the presence of those gases and vapours which prevent the oxidation of phosphorus have no effect on its vaporisation. Qualitative experiments are carried out with a large number of organic vapours to investigate the cause of their negative catalytic action on the oxidation of phosphorus. It is shown that the iodine substitution products are particularly active in this respect; the action is attributed to the presence of free iodine, for it is shown that iodine itself has the same action. Two substances, nitrobenzene and diphenylamine, work positively in catalysing the oxidation of phosphorus. If a drop of these substances is brought in contact with phosphorus in air, the glow is strengthened, and almost immediately the phosphorus bursts into flame. J. F. S.

Oxidation of Arsenious and Antimonious Oxides. PERCY EDGERTON (*J. Amer. Chem. Soc.*, 1913, **35**, 1769—1770).—In contradistinction to Tingle (A., 1911, ii, 1086), the author finds that arsenious and antimonious oxides do not undergo oxidation when aqueous-alcoholic solutions are boiled for some time. T. S. P.

Boron Hydrides. III. Solid Boron Hydrides; the Hydride B_2H_6. ALFRED STOCK, KURT FRIEDERICI, and OTTO PRIESS (*Ber.*, 1913, **46**, 3353—3365).—It has already been shown (Stock and Friederici, this vol., ii, 699) that the boron hydride, B_4H_{10}, is readily decomposed at 100°, with the formation of the hydride, B_2H_6. This decomposition also takes place, but not so readily, under the action of ultra-violet light.

In addition to the properties of the hydride, B_2H_6, which have already been given (*loc. cit.*), other properties are mentioned in this paper. Among these may be noted: m. p. −169°; in the presence of air it gives solid boron compounds containing oxygen; it reacts with bromine (in carbon disulphide solution), but not with dry hydrogen chloride; with water it reacts so much more slowly than the hydride, B_4H_{10}, that a mixture of the two gases may be analysed by treatment with water.

When the hydride, B_4H_{10}, is heated for four to five hours at 100°, or the hydride, B_2H_6, for forty-eight hours at 115—120°, a volatile solid *hydride*, $B_{10}H_{14}$, is formed, together with a non-volatile, colourless, solid *hydride*, and a non-volatile, yellow *hydride*.

The hydride, $B_{10}H_{14}$, is a colourless substance, with a penetrating, peculiar odour, which is not similar to that of the gaseous hydrides. It sublimes in a vacuum, giving centimetre-long needles, or else compact crystals, m. p. 99·5°, D 0·94. Decomposition of the fusion commences at 200°, and at higher temperatures yellow products are formed. The vapours can be heated at 400° for a short time without appreciable decomposition, but at 600—700° decomposition into boron and hydrogen takes place. No decomposition of the solid substance takes place on exposure to the air, although the

vapours slowly react, giving the odour of B_4H_{10}. It is not attacked by water, even by boiling water, but dissolves in sodium hydroxide, giving an intense yellow solution. When kept for several days at room temperature, in the absence of air, some decomposition takes place.

The two non-volatile solid hydrides mentioned above can be separated from each other by the fact that the colourless hydride is soluble in carbon disulphide, the yellow hydride being insoluble. The former probably contains 12 atoms of boron to the molecule; it is stable towards water, and dissolves in sodium hydroxide to a yellow solution. On heating at 150° it gives the yellow hydride, which is soluble, with decomposition, in water, and probably has the atomic ratio 5B : 4H.

In the course of the investigation, other boron hydrides have been detected, but they have not yet been sufficiently investigated.

T. S. P.

The Hydrothermal Formation of Silicates. PAUL NIGGLI and GEORGE W. MOREY (*Zeitsch. anorg. Chem.*, 1913, **83**, 369—416).—A review of previous work on the hydrothermal formation of silicates, including theoretical discussions of the equilibrium in aqueous solutions above 300°. Definite quantitative data are very scanty. A bibliography, including the principal data from each memoir cited, is included, together with a tabular index according to mineral names.

C. H. D.

The Reaction between Sulphur and Potassium Hydroxide in Aqueous Solution. HERMAN V. TARTAR (*J. Amer. Chem. Soc.*, 1913, **35**, 1741—1747).—The primary reaction of sulphur with potassium hydroxide in hot aqueous solutions takes place in accordance with the equation: $6KOH + 8S = 2K_2S_3 + K_2S_2O_3 + 3H_2O$. When sulphur is used in excess, a secondary reaction occurs, in which it combines with the trisulphide to form the pentasulphide. Potassium tetrasulphide is perhaps formed as an intermediate product. Variation in temperature (below 100°) and concentration does not alter the nature of the reaction.

In the analysis of the various solutions, the potassium in the form of thiosulphate, and the sulphur present as polysulphide, as thiosulphate, as sulphite, and as sulphate were estimated according to the methods given by Haywood (A., 1905, ii, 312). The estimation of potassium present as polysulphide was carried out by precipitation with a standard ammoniacal solution of zinc chloride, when zinc polysulphide is precipitated (compare Tartar, *J. Ind. Eng. Chem.*, 1910, **2**, 271).

T. S. P.

A Family of Metallic Phosphides Derived from Hydrogen Phosphide, P_2H_5. ROBERT BOSSUET and LOUIS HACKSPILL (*Compt. rend.*, 1913, **157**, 720—721. Compare A., 1912, ii, 252).—Rubidium phosphide dissolves in liquid ammonia to a yellow limpid solution, which on evaporation at −18° deposits transparent, yellow crystals having the constitution $Rb_2P_5,5NH_3$, and efflorescing with loss

of their ammonia at the ordinary temperature. This alkaline phosphide in solution in liquid ammonia reacts with solutions of nitrates of barium, strontium, calcium, silver, copper, and lead in the same solvent, giving amorphous precipitates, yellow in the case of the alkaline earth metals, brown for silver, and black for the others. The precipitates only deposit slowly, and are very readily oxidised in the air. The authors succeeded in isolating and analysing the *lead phosphide*, finding it to have the constitution PbP_5, thus giving indication of a series of such phosphides of bivalent metals having the constitution MP_5. When heated in a vacuum at 400°, lead phosphide loses its phosphorus, leaving metallic lead. The phosphide burns spontaneously in air, is attacked slowly by water, with dilute sulphuric and hydrochloric acids gives solid hydrogen phosphide and the salts of lead, and with dilute nitric acid it yields lead nitrate and phosphoric acid.

W. G.

Hydraulic Lime Containing Magnesia. I. Thermal Decomposition of Normal Dolomite. O. KALLAUNER (*Chem. Zeit.*, 1913, **37**, 1317).—Dolomite is sensibly decomposed at about 500°. The velocity of decomposition increases slowly at first, more rapidly above 650°, and reaches its first maximum at 710—730°. Above this temperature, it again increases slowly up to 870°, then more rapidly, and attains a second maximum between 900° and 915°. The presence of free lime was first observed in the aqueous extract of the product which had been heated at 875° during fifteen minutes. The conclusion is drawn that the double salt is decomposed into its components to an appreciable extent at 500°, and that the process attains its maximum velocity at 710—730°, whilst, further, the liberated magnesium carbonate immediately breaks down into magnesium oxide and carbon dioxide. The residual calcium carbonate begins to decompose at 875°, and this process reaches its maximum velocity at 900—915°. H. W.

Atomic Weight of Barium. WILLIAM ŒCHSNER DE CONINCK (*Rev. gen. Chim. pure appl.*, 1913, **16**, 245).—Pure barium carbonate was prepared by the action of sodium carbonate on barium chloride, when analysis indicated a purity of 99·998%; this was decomposed by nitric acid, and the evolved carbon dioxide weighed. From these results the molecular weight of $BaCO_3$=197·36, of BaO=153·36, and the atomic weight of Ba=137·36. F. M. G. M.

The Optical Orientation of Some Cast Metals. KURD ENDELL and H. HANEMANN (*Zeitsch. anorg. Chem.*, 1913, **83**, 267—274).—Some cast metals have been examined by reflecting polarised light from their polished surface and passing it through a quartz plate and analyser. Anisotropy of the reflecting metal is easily detected in this way. In another modification of the method, ordinary light is used, which is examined after reflexion by means of a Savart plate, which shows interference bands when the metal is anisotropic.

The metals are fused in small porcelain crucibles and cooled in air. Sections are then cut at several angles and polished, but not etched.

Zinc and antimony crystallise, like ice, in similarly orientated crystals, perpendicular to the cooling surface. Stirring during cooling gives an aggregate of irregular orientation, and this result only is obtained with bismuth and tin. When an anisotropic metal is present, together with a eutectic, the primary crystals are in some cases similarly orientated, and in other cases not so.

Cementite in steel is anisotropic, as are sulphide enclosures, and also iron phosphide and silicide, and 80% ferromanganese. Silicate slag enclosures are isotropic. Anisotropy has not been detected in cold worked steel.

C. H. D.

The Binary Systems Zinc-Tin, Zinc-Cadmium, and Tin-Cadmium, and the Ternary System Zinc-Tin-Cadmium. RICHARD LORENZ and D. PLUMBRIDGE (*Zeitsch. anorg. Chem.*, 1913, **83**, 228—242).—The three binary systems are of a simple type, and the freezing-point curves are in good agreement with previous determinations. The eutectic point Sn–Zn is found at 13·5 atomic % Zn and 199°, of Cd–Zn at 27 atomic % Zn and 264°, and of Sn–Cd at 29 atomic % Cd and 177°. Solid solutions are formed in the last series up to 2 atomic % Cd. The first series is free from solid solutions, and the second only contains them to a very limited extent.

The ternary system is of a very simple type, with three freezing-point surfaces, of which that which corresponds with the crystallisation of zinc is much the largest. The ternary eutectic contains 70·83 atomic % of tin, 25·41% of cadmium, and 3·70% of zinc, and freezes at 164°.

Microscopical examination confirms the thermal results.

C. H. D.

Arsenides of Cadmium. SERGEI F. SHEMTSCHUSHNI (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1137—1155).—The author has made a systematic investigation, by means of the melting-point method and of the microstructure, of the system cadmium–arsenic. The alloys were prepared by fusing cadmium beneath a layer of mixed lithium and potassium chlorides and gradually adding coarsely ground arsenic; by this means volatilisation of the arsenic is minimised, and mixtures with large proportions of arsenic can be obtained.

The results obtained indicate the existence of the two compounds Cd_3As_2 and $CdAs_2$, and are confirmed by the curves of specific gravity and atomic volume, each of these consisting of three rectilinear branches meeting at points corresponding with the above two compounds. Both compounds are formed with increase of volume, and have the specific gravities 6·25 and 5·86 respectively, whilst those calculated according to the law of mixtures are 7·47 and 6·69. The relatives values of the hardness of the compounds and their constituents are: cadmium, 2; Cd_3As_2, less than 3·5; arsenic, 3·5; $CdAs_2$, 3·5—4.

From the configuration of its crystals in conjunction with its composition, the compound $CdAs_2$ may be regarded as probably belonging to the pyrites type. T. H. P.

The Scientific Foundations of Furnace (Roasting) Operations. RUDOLF SCHENCK (*Zeitsch. angew. Chem.*, 1913, **26**, 646—652).—A lecture delivered before the Verein deutscher Chemiker at Breslau in September, 1913, dealing with the results hitherto obtained in the roasting of lead and copper sulphide ores.

T. S. P.

Decomposition of Sparingly Soluble Lead Salts. FRIEDRICH AUERBACH and HANS PICK (*Zeitsch. Elektrochem.*, 1913, **19**, 827—830).—The conditions of stability of basic lead carbonate in the presence of sodium carbonate, sodium hydrogen carbonate, and sodium sulphate have been worked out at 18° and 37°. The results are plotted on spatial diagrams, in which it is shown that a double salt of basic lead carbonate and sodium carbonate of the formula $3PbCO_3,Pb(OH)_2,Na_2CO_3$ is formed as a greyish-yellow powder when the concentration of sodium carbonate slightly exceeds $0{\cdot}1N$. This compound is decomposed by water into white basic lead carbonate and sodium carbonate. Similar investigations were made with lead chromate and its basic salts; it is shown that a similar spatial diagram can be drawn to represent the regions of existence of lead chromate and its basic salts. The diagram for lead chromate differs from that of lead carbonate, inasmuch that in the latter case there is only a small region in which the normal lead carbonate is stable, whilst in the former case the stability region of lead chromate is very wide. J. F. S.

Change of Properties in the Polymorphic Transformations of Thallium, Tin, Zinc, and Nickel. (MAX WERNER (*Zeitsch. anorg. Chem.*, 1913, **83**, 275—321).—The transformation curve of thallium has been determined up to 3000 kg. per cm.^{2}, and within this range the temperature of transformation is lowered by pressure in an almost linear manner, the lowering being 6° for an increase of 3000 kg. per cm.^{2} The volume change is 0·000044 c.c. per gram, from which the value $0{\cdot}26 \pm 0{\cdot}07$ cal. per gram is calculated for the heat of transformation, whilst Tammann's method gives 0·2 cal. The electrical conductivity of thallium wire prepared by extrusion undergoes a sudden change at the transformation temperature. The recrystallisation of the metal hardened by extrusion takes place above the transformation temperature. The two modifications have different temperature-coefficients of conductivity. There is a slight discontinuity in the thermoelectric force against copper at 226°.

A transformation of tin has been detected at 168° under 100 kg. per cm.^{2}. This corresponds with the values obtained under different pressures by other workers, but the transformation is often suppressed. A p-T diagram is constructed from the existing data. The heat of transformation of tetragonal into rhombic tin is

0·02 cal. per gram, and the volume change 0·00017 c.c. per gram. The electrical resistance undergoes a change at 161°, but the thermal effect is too small to be detected with the apparatus used. The thermoelectric force of a tin–nickel couple shows a break at the same temperature.

A thermal effect in zinc has been detected at 304°, but not at 170°. The same result is obtained by an examination of the electrical resistance, and of the thermoelectric force measured against iron or platinum. A determination of the upper limit of elasticity also fails to show any discontinuity of the properties of zinc at 170°.

The heat of transformation of nickel at 352° is determined from the cooling curves to be 0·013 cal. per gram. The electrical resistance and the thermoelectric force measured against copper indicate a break at 355—365°. This is also the temperature of the magnetic change. A volume change does not occur, and the transformation temperature is the same for hard and soft wires.

The bearing of these results on the explanation of the re-crystallisation of hardened metals is discussed. C. H. D.

Rapid Refining of Copper with a Rotating Cathode. CHARLES W. BENNETT and C. O. BROWN (*J. Physical Chem.*, 1913, 17, 685—694).—An apparatus is described by which the electrolytic refining of copper can be demonstrated to students. The apparatus works at 65 amperes per sq. dcm. of cathode surface, and by its means 100 grams of copper can be deposited in an hour. Experiments are described in which the usual impurities of copper are separated from artificially prepared anodes. Working scale drawings are given of the apparatus. The rotating cathode makes about 5000 revolutions per minute, and is made of aluminium.

J. F. S.

Apparatus for the Purification of Mercury by Distillation in a Vacuum. BERTRAM LAMBERT (*Chem. News*, 1913, 108, 224—225). —The apparatus described by the author does not differ in principle from the ordinary apparatus, which makes use of the barometric method for maintaining a vacuum. T. S. P.

Theory of the Preparation of Aluminium. RICHARD LORENZ, ASMUS JABS and W. EITEL (*Zeitsch. anorg. Chem.*, 1913, 83, 328)—A correction. The eutectic proportions given (this vol., ii, 963) contain a numerical error. They should be 13·6% of aluminium fluoride and 86·4% sodium fluoride, in good agreement with the values found by Fedotéev and Iljinsky (this vol., ii, 324).

C. H. D.

Action of Three % Hydrogen Peroxide Solution on Aluminium. DROSTE (*Chem. Zeit.*, 1913, 37, 1317).—The corrosion of an aluminium beaker, which had contained 3% hydrogen peroxide solution for a short period, has led the author to examine the action of the latter on a sample of aluminium containing Al 99·46%,

Fe 0·03%, Si 0·51%. The metal is rapidly dissolved with the exception of a few black specks, which consist of aluminium, to which silicon adheres. The white precipitate which is formed has, when air-dried, the composition $Al_2(OH)_6,2H_2O$. Soluble colloidal aluminium hydroxide does not appear to be formed. Aluminium vessels are thus unsuitable for liquids which contain or can form free oxygen or ozone. H. W.

The Binary System Aluminium-Tin. RICHARD LORENZ and D. PLUMBRIDGE (*Zeitsch. anorg. Chem.*, 1913, **83**, 243—245).—Freezing-point determinations and microscopical examination confirm the conclusions of Gwyer (A., 1906, ii, 544) that solid solutions are not formed in this system, and that the eutectic point is at 98 atomic % Sn (compare Shepherd, A., 1904, ii, 486). C. H. D.

The Presence of Gallium in Commercial Aluminium and its Separation. CH. BOULANGER and J. BARDET (*Compt. rend.*, 1913, **157**, 718—719).—The authors have proved the presence of gallium in several specimens of commercial aluminium by spectrographic methods, and in one case have isolated it in the form of its oxide, finding 0·017% of gallium in the commercial metal. Specimens of bauxite similarly examined were also found to contain aluminium. W. G.

Alloys of Manganese and Cobalt. KARL HIEGE (*Zeitsch. anorg. Chem.*, 1913, **83**, 253—256).—Manganese and cobalt form a continuous series of solid solutions, the freezing-point curve passing through a flat minimum at about 30% of cobalt and 1150°. The crystals are not homogeneous, but become more nearly so after annealing in magnesia at 1000° for five hours. The magnetic transformation curve falls with increasing manganese, in almost linear fashion. C. H. D.

Manganese Carbides, and Their Preparation by Heating the Metal in a Current of Methane. SIEGFRIED HILPERT and J. PAUNESCU (*Ber.*, 1913, **46**, 3479—3486).—When finely powdered manganese is treated with methane, or with a mixture of methane and hydrogen, at 600—900°, carbides are formed (compare Hilpert and Ornstein, this vol., ii, 604). In pure methane, carbides containing over 20% of carbon were obtained, and in mixtures of equal volumes of hydrogen and methane, carbides containing up to 15% of carbon. The limiting amounts of carbon taken up at the various temperatures do not, however, correspond with simple stoicheiometric proportions.

When the carbides contain 8% or less of carbon, treatment with dilute acids gives nearly all the carbon as methane; very little ethylene and no acetylene is evolved. With more than 8% of carbon, fatty substances and spongy carbon are produced. The conclusion is therefore drawn that the carbides are not derivatives of simple hydrocarbons, as are the carbides of calcium and aluminium.

The carbides are, to a great extent, ferromagnetic. Magnetic properties are evidenced with 1% C, and reach a maximum at about 4% C. Carbides containing more than 7% C are not ferromagnetic. T. S. P.

Structure and Properties of Alloys Prepared by Fusing Together Iron and Zinc Under Pressure. U. RAYDT and GUSTAV TAMMANN (*Zeitsch. anorg. Chem.*, 1913, **83**, 257—266).—The alloys of iron and zinc have hitherto been examined only as far as 24% of iron, richer alloys having too high a vapour pressure (von Vegesack, A., 1907, ii, 170). The entire series has now been investigated by using a closed furnace, in which a pressure of 110—130 atmospheres could be obtained. The electric furnace is made up of carbon rods, 3 mm. diameter, connected by iron plates to form a conductor bent repeatedly on itself. This heater surrounds a magnesia cylinder, and requires 25—30 amperes to reach 1500°. Compressed hydrogen is admitted to the bomb after the metals have been enclosed in a porcelain tube. The composition of the alloys is determined by analysis after fusion. The structure has been examined microscopically, but the freezing-point curve of the alloys rich in iron has not been determined.

No compounds, other than those formed under atmospheric pressure, $FeZn_7$ and $FeZn_3$, have been recognised. The only other micrographic constituent is a solid solution of zinc in iron, the saturation point of which appears to lie at about 80% of iron. The temperature of magnetic transformation falls with increasing zinc content, and is then constant at 650° from 80 to 22% of iron. A hypothetical diagram is constructed in accordance with these facts. An alloy with 96% of iron is malleable when cold, although more brittle than iron, but the alloy with 80% is brittle and not malleable at the ordinary temperature. C. H. D.

Precipitation of Iron by Light and Green Aquatic Plants. HANS MOLISCH (*Zeitsch. Kryst. Min.*, 1913, **53**, 92; from *Sitzungsber. Akad. Wiss. Wien, math.-naturw. Klasse*, 1910, **109**, 959—983).—Ferric hydroxide is precipitated by the action of light on certain dilute solutions containing salts of iron; for example, iron ammonium citrate; whilst a solution of ferrous sulphate and ferrous hydrogen carbonate deposits ferric hydroxide on remaining even in the dark. Green aquatic plants under the influence of light also favour the deposition of iron from solution, since they extract alkalis and carbon dioxide and give off oxygen. L. J. S

Anhydrous Sulphates. VI. Cobaltous Sulphate with Lithium Sulphate, Sodium Sulphate, and Potassium Sulphate. GENNARO CALCAGNI and D. MAROTTA (*Gazzetta*, 1913, **43**, ii, 380—390. Compare A., 1912, ii, 761, 918, 1064).—Lithium sulphate and cobaltous sulphate do not form any compounds, but exhibit a restricted field of mixed crystals from about 100—83% Li_2SO_4; there is an eutectic corresponding with 595° and 63% Li_2SO_4.

Cobaltous sulphate and sodium sulphate form a compound.

$CoSO_4,3Na_2SO_4$, which decomposes above 425°; at concentrations from 100% to 67% Na_2SO_4, mixed crystals are formed, and there is an eutectic corresponding with 575° and 50% of either component.

Cobaltous sulphate and potassium sulphate yield a rather complicated thermal diagram. Two compounds are formed, both being already known. The compound, $CoSO_4,K_2SO_4$, decomposes above 500°. The compound, $2CoSO_4,K_2SO_4$, crystallises at 736°, and there is an eutectic at about 725° (about 31% K_2SO_4). At 535° there is an eutectic corresponding with 60% K_2SO_4. R. V. S.

Ternary Alloye of Nickel, Copper, and Silver. PIETRO DE CESARIS (*Gazzetta*, 1913, **43**, ii, 365—379).—This paper records in tables, curves, and photomicrographs the results obtained by the application of the method of thermal analysis to this system. In some cases, experiments were also made with mixtures containing two only of the constituents, although the three binary systems involved have previously been investigated by other authors.

R. V. S.

The Nature of Auxiliary Valencies. V. The Influence of the Anion on the Stability of Complex Catione. FRITZ EPHRAIM (*Ber.*, 1913, **46**, 3103—3113. Compare this vol., ii, 496). —In the former paper the dissociation temperatures of the ammines of the sulphates of several bivalent metals were discussed. In the present instance the same function of the ammines of different salts of nickel has been studied. As a general rule it is found that the nickel salts of the stronger acids unite more firmly with ammonia than do the salts of weak acids. The following descending order of stability is established: perchlorate, iodide, bromide, chlorate, nitrate, dithionate, chloride (hexammines), formate (tetrammine), sulphate (hexammine), thiosulphate (pentammine), tetrathionate (hexammine), nitrate (pentammine), hypophosphite (hexammine), acetate (? tetrammine), formate and thiocyanate (hexammines).

In most cases the stability of the ammine is parallel to the stability of the corresponding ammonium salt; for example, the hexammine of nickel iodide and ammonium iodide decomposes at higher temperatures than the bromides or chlorides. The more stable ammines are also the least soluble in water.

The following new compounds are described: *Nickelhexammine nitrate*, $Ni(NO_3)_2,6NH_3$, prepared by the action of dry ammonia on anhydrous nickel nitrate; *nickelhexammine chlorate*, precipitated in blue, glistening crystals by ammonia gas from a very concentrated solution of nickel chlorate; *nickelpentammine thiosulphate*, $NiS_2O_3,5NH_3,H_2O$, precipitated in blue leaflets by ammonia from concentrated solutions of nickel thiosulphate; loses water when heated in a stream of ammonia; *nickelhexammine tetrathionate*, precipitated as a white oil, which soon solidifies to small, pale violet needles when alcohol is added to a solution of nickel tetrathionate and ammonia; stable when dry, decomposes when moist; *nickelpentammine nitrite*, a blue compound obtained by treating

the red tetrammine with dry ammonia; *nickelhexammine hypophosphite*, a reddish-violet salt, prepared by passing a slow stream of ammonia over anhydrous nickel hypophosphite; some particles remain unattacked, but with a stronger stream of gas the reaction is too vigorous; *nickelhexammine formate*, violet, prepared by treating nickel formate, dried at 140°, with ammonia, when the pale blue tetrammine is soon formed, whilst the final addition is very slow. J. C. W.

Alloys of Molybdenum and Cobalt. U. RAYDT and GUSTAV TAMMANN (*Zeitsch. anorg. Chem*, 1913, **83**, 246—252).—Molybdenum (98·2%), prepared by the aluminothermic process from molybdenum trioxide, is alloyed with cobalt (98%), prepared by repeatedly re-melting cobalt cubes in a magnesia vessel with fragments of porcelain. This cobalt has m. p. 1480°. Alloys with up to 65% Mo may be prepared by heating at 1800° in magnesia tubes; further quantities of molybdenum are not completely dissolved at that temperature. The freezing-point curve shows a eutectic point at 38% Mo and 1335°. Solid solutions are formed to 28% Mo. From the eutectic point the freezing-point curve rises, and has a break at 1484°, corresponding with the compound MoCo, which does not form solid solutions. There is no indication of any further compound. The compound is non-magnetic, but the solid solution rich in cobalt is magnetic, the temperature of the transformation, which is reversible, falling from 1143° for pure cobalt to about 760° for the saturated solid solution. The crystals of the latter show marked coring under the microscope. The compound MoCo crystallises in long needles. The free molybdenum forms rounded crystallites.

Alloys richer in molybdenum may be prepared by the aluminothermic method, but then always contain aluminium. C. H. D.

Colour Changes in Colloidal Gold. S. H. LONG (*Proc. Univ. Durham Phil. Soc.*, 1913, **5**, 113—118).—Colloidal gold solutions of a red, blue, and purple colour have been prepared by the use of a high frequency alternating arc (compare this vol., ii, 1033). The behaviour of these solutions in an electrical field was investigated. The red colloid moves towards the cathode, but if the field is allowed to act for some time, the colloid turns blue and moves towards the anode. The blue colloid migrates to the anode, and no further change occurs when the action of the field is prolonged for about two hours. The purple colloidal solutions show both these effects, and this indicates that these contain both the red and blue colloids.

It is supposed that the red colloid consists of positively charged particles associated with hydroxyl ions, and the blue colloid of negatively charged particles surrounded by hydrogen ions. The fact that the red colloid is converted into the blue by the action of electrolytes or of an electric field indicates that the blue represents the more stable modification. H. M. D.

Alloys of Palladium with Nickel. Fritz Heinrich (*Zeitsch. anorg. Chem.*, 1913, **83**, 322—327).—Palladium and nickel form a continuous series of solid solutions, the freezing-point curve having a flat minimum near 1208°. The curve is very asymmetrical, and there are indications of an unstable phase. The magnetic change curves fall with increasing percentages of palladium, slowly at first, rapidly beyond 40% Pd, and at about 80% Pd the temperatures of the change observed on heating and on cooling become identical. The alloys are homogeneous on etching. C. H. D.

Mineralogical Chemistry.

Iron Mines near Borossebes, Hungary. J. Balás (*Zeitsch. Kryst. Min.*, 1913, **53**, 65; from *Bányász. és Kohászati Lapok*, 1910, xliii *Jahrg.*, **51**, 144—156).—Iron ore soccur in Triassic dolomite in the Kodru Mountains, in comitat Arad. They consist of brown and red ironstone (limonite and hæmatite), and are associated with pyrolusite, manganite, and psilomelane. The iron ores contain 25·18—47·83% Fe with 3·71—29·12% Mn; and the manganese ores contain 42·34—47·82% Mn with 15·16—19·08% Fe. L. J. S.

Synthesis of Wulfenite. Emil Dittler (*Zeitsch. Kryst. Min.*, 1913, **53**, 158—170).—Wulfenite occurs as a mineral of secondary origin in the upper oxidised zone of veins of lead ore, and is frequently associated with cerussite, molybdic-ochre, limonite, and corroded galena. The red crystals from Arizona melt at 1060—1070° without destruction of the colour (which is therefore not organic). Experiments were made to determine the action of various gases and solutions on the mineral. It is readily attacked by hydrogen sulphide in water, and by digestion with sodium carbonate solution. In the latter case the product consists of hexagonal scales of hydrocerussite, $Pb(Pb{\cdot}OH)_2(CO_3)_2$. This compound, after long digestion with a dilute alkaline solution of ammonium molybdate, gives small, tetragonal crystals of wulfenite, $PbMoO_4$. The amorphous precipitate obtained by mixing solutions of lead chloride and ammonium molybdate becomes crystalline on heating, and has the composition $2PbO,5MoO_3$.
L. J. S.

Custerite, a New Contact-metamorphic Mineral. J. B. Umpleby, Waldemar T. Schaller, and Esper S. Larsen (*Amer. J. Sci.*, 1913, [iv], **36**, 385—394).—As finely granular masses resembling green marble in appearance, this mineral is found in the contact zone between marble aud garnet-diopside-magnetite rock around large inclusions of limestone in granite-porphyry, near Mackay, in Custer Co., Idaho. Microscopical examination of thin sections points to monoclinic symmetry with basal and prismatic cleavages and lamellar twinning. Refractive indices: $\alpha=1{\cdot}586$, $\beta=1{\cdot}589$,

$\gamma = 1{\cdot}598$; $H = 5{-}6$, $D = 2{\cdot}91$. When gently heated, the material phosphoresces with a golden-yellow light. It fuses with difficulty to a white enamel, and is readily decomposed by acids, with the separation of gelatinous silica. Analysis gave:

SiO_2.	CaO.	H_2O.	F.	MgO.	Magnetite.	Total (less O for F).
32·17	55·11	5·30	8·12	1·19	1·00	99·47

The formula is $Ca_2SiO_3(OH,F)_2$. No water is given off at 110°, and in water the mineral immediately gives a deep red colour with phenolphthalein, suggesting the presence of the group (CaOH). The formula is therefore written structurally as a metasilicate, $SiO_3(CaOH)(CaF)$. Allied minerals are zeophyllite ($Ca_4Si_3H_4F_2O_{11}$), cuspidine ($Ca_4Si_2F_2O_7$), and hillebrandite ($Ca_2SiO_3(OH)_2$). The relations of these are discussed, and various structural formulæ are suggested. L. J. S.

Minerals from the Kinzig Valley, Baden. V. DÜRRFELD (*Zeitsch. Kryst. Min.*, 1913, **53**, 182—183).—Crystals of fluorite are described from Artenberg, near Steinach. Crystals of prehnite, pectolite, datolite, and apophyllite occur in drusy cavities in amphibolite at Haslach. The pectolite has the form of fine needles, with a radially-fibrous structure and a snow-white to pale greenish-white colour. Analysis gave:

SiO_2.	Al_2O_3.	CaO.	Na_2O.	K_2O.	H_2O.	Total.
52·71	2·52	33·95	9·53	0·18	1·92	100·81

For a new hydrous vanadate of lead and zinc, previously described (V. Dürrfeld, *Zeitsch. Kryst. Min.*, 1912, **51**, 278) as occurring in orange-yellow to yellowish-brown, monoclinic needles on decomposed galena at Reichenbach, near Lahr, the name *hügelite* is now proposed. L. J. S.

Chemical Constitution of the Sodalite and Nephelite Groups. SILVIA HILLEBRAND (*Zeitsch. Kryst. Min.*, 1913, **53**, 92; from *Sitzungsber. Akad. Wiss. Wien*, *math.-naturw. Klasse*, 1910, **109**, 775—806).—The silicic acid isolated by Tschermak's method from the sodalite of Lake Baikal contains 37·96 and 37·24% H_2O (H_2SiO_4 requires 37·40%). The minerals of the sodalite group are therefore regarded as compounds of the orthosilicate, $Na_3Al_3Si_3O_{12}$, with NaCl, Na_2SO_4, $CaSO_4$, and probably Na_2S_3.

The silicic acid isolated from the nephelite of Miass contained 37·34 and 36·38% H_2O, and from the elæolite of Mariapol 35·40%. The predominating constituent of these minerals is thus the orthosilicate, $Na_3Al_3Si_3O_{12}$; and mixed with this are the isomorphous potassium and calcium compounds, $K_3Al_3Si_3O_{12}$ and $NaCaAl_3Si_3O_{12}$, together with a potassium compound richer in silica, $K_2Al_2Si_4O_{12}$. L. J. S.

The Rhyolite Kaolins of Hungary. L. PETRIK (*Zeitsch. Kryst. Min.*, 1913, **53**, 64—65; from *Magyar Üveg- és Agyagujság*, 1910, **10**, No. 5, 2—3, No. 6, 2—3, No. 8, 4—5).—The white china-clays

from various localities in Hungary have been derived from trachytic and rhyolitic rocks. Several analyses are given of the raw and washed material. These vary widely in composition, containing 32·32—81·91% of the clay substance, 1·85—54·99% quartz sand, and 0—56·20% felspar sand. The clay substance approximates in some cases to the kaolinite formula $H_4Al_2Si_2O_9$, but in others there is a considerable excess of alumina and water, due to the presence of freely soluble aluminium hydroxide. L. J. S.

Garnets from the Volcanic Rocks and Bombs of the Lower Rhine District. JOHANNES UHLIG (*Zeitsch. Kryst. Min.*, 1913, **53**, 203—208; from *Verh. Nat. Ver. preuss. Rheinlande u. Westfalens*, 1910, **67**, 307—403).—Garnets of several types were analysed in detail especially for the presence of rarer elements.

I. Melanite as loose crystals in leucite-tuff from the Perlerkopf in the Laach district. To bring this analysis into agreement with the garnet formula, the figures are readjusted as TiO_2, 4·45; Ti_2O_3, 3·36; Fe_2O_3, 21·65; FeO, nil.

II. Opaque, brown aplome in a bomb from Laach.

III. Pale blood-red almandine in muscovite-schist from Dachsbusch, Laach.

IV. Pale rose-red almandine in sillimanite-biotite rock from Laach.

V. Almandine in a cordierite-garnet rock from Laach.

VI. The red nucleus of the same with the black, slaggy shell removed as far as possible.

VII. Almandine as grains enclosing fine needles of titanite; to agree with the garnet formula the iron is readjusted as Fe_2O_3, 1·69; FeO, 24·14.

VIII. Wax-yellow grossularite, occurring as enclosures in basalt at Finkenberg, near Bonn.

IX. Brownish-red hessonite from the same occurrence.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
SiO_2	32·71	36·64	37·55	37·13	40·25	41·50	39·73	40·73	38·68
TiO_2	8·30	0·56	0·45	0·48	0·39	0·56	0·19	0·85	0·39
Al_2O_3	5·72	11·01	20·86	20·91	21·21	21·36	20·23	19·72	18·42
Fe_2O_3	17·91	15·66	0·66	1·16	2·21	—	2·94	2·39	5·30
V_2O_3	0·24	0·09	—	0·01	trace	—	trace	n.d.	trace ?
Cr_2O_3	trace	—	—	—	0·06	—	0·03	—	—
Ce_2O_3	—	0·09	—	—	—	—	—	—	—
FeO	3·36	1·16	26·77	33·22	26·66	23·74	23·01	0·92	2·52
NiO	trace	trace	—	trace	0·01	—	0·05	—	trace?
CoO	—	—	—	—	trace?	· ·	trace	—	—
MnO	0·52	1·99	6·85	4·89	0·73	0·83	0·65	0·58	0·66
MgO	1·33	0·44	4·80	1·23	6·95	7·47	6·94	2·54	0·79
CaO	29·25	30·15	2·28	1·60	0·71	0·76	6·09	32·10	32·59
Na_2O	—	0·87	—	—	0·31	—	—	—	—
K_2O	—	0·30	—	—	0·30	—	—	—	—
H_2O (over 125°)	0·32	0·87	0·27	0·18	0·37 }	0·76	0·70 }	1·18	0·40
H_2O (hygrosc.)	0·19	0·32	0·11	0·07	9·07 }		0·23 }		0·39
Total	99·85	100·15	100·60	100·98	100·73		100·79	101·01	100·14
Sp. gr.	3·692	3·581	4·084	4·158	3·926		3·907	3·470	3·566

To express the percentages of the several isomorphous molecules

of the garnet group that enter into the composition, the following nomenclature is used. The lime-garnets are written as $(Al) = Ca_3Al_2Si_3O_{12}$, $(Fe) = Ca_3Fe_2Si_3O_{12}$, $(Ti) = Ca_3Ti_2Si_3O_{12}$, $(V) = Ca_3V_2Si_3O_{12}$, etc.; and the remaining garnets as $Fe = Fe_3Al_2Si_3O_{12}$, $Mg = Mg_3Al_2Si_3O_{12}$, $Mn = Mn_3Al_2Si_3O_{12}$, $Na = Na_6(Al,Fe)_3O_{12}$.

The analyses correspond with:

		$RO_2 : R_2O_3 : (RO + R_2O)$.
I.	$(Fe)_{62 \cdot 6}(Al)_{19 \cdot 7}(Ti)_{10 \cdot 7}(V)_{0 \cdot 8}Mg_{5 \cdot 1}Mn_{1 \cdot 1}$	3 : 1·08 : 2·82
II.	$(Fe)_{47 \cdot 4}(Al)_{40 \cdot 5}(V)_{0 \cdot 3}(Ce)_{0 \cdot 1}Mn_{4 \cdot 5}Fe_{2 \cdot 6}Mg_{1 \cdot 8}Na_{2 \cdot 8}$.	2·97 : 1 . 2·96
III.	$Fe_{59 \cdot 2}Mg_{19 \cdot 0}Mn_{15 \cdot 4}(Al,Fe)_{6 \cdot 4}$	3·01 : 1 : 3·02
IV.	$Fe_{78 \cdot 9}Mn_{11 \cdot 1}Mg_{5 \cdot 0}(Al)_{4 \cdot 7}$	3·03 : 1 : 2·96
V.	$Fe_{65 \cdot 5}Mg_{30 \cdot 4}Mn_{1 \cdot 8}(Al,Fe,Cr)_{2 \cdot 2}$	3·06 : 1 : 2·59
VII.	$Fe_{53 \cdot 6}Mg_{27 \cdot 5}Mn_{1 \cdot 5}(Al,Fe,Cr)_{17 \cdot 4}$	3·04 : 1 : 2·82
VIII.	$(Al)_{79 \cdot 3}(Fe)_{7 \cdot 2}Mg_{10 \cdot 1}Fe_{2 \cdot 1}Mn_{1 \cdot 3}$	3·13 : 0·95 : 3
IX.	$Al_{74 \cdot 6}Fe_{15 \cdot 5}Fe_{5 \cdot 5}Mg_{3 \cdot 1}Mn_{1 \cdot 5}$	3·03 : 1 : 3·03

From these analyses it is seen that amongst the lime-garnets those richer in iron (lime-iron garnets) contain correspondingly less of the iron-alumina, magnesia-alumina, and manganese-alumina molecules.

L. J. S.

The Garnet Group. HENDRIK E. BOEKE (*Zeitsch. Kryst. Min.*, 1913, **53**, 149—157. Compare preceding abstract).—The ratios of the various bases taken from 261 published analyses of garnets are plotted on diagrams. No. 1 includes garnets poor in lime; the percentages of magnesia, ferrous oxide, and manganous oxide are increased to a total of 100, and are plotted on triangular co-ordinates with MgO, FeO, MnO 100% at each of the three corners. In No. 2, Fe_2O_3 and Al_2O_3 are increased to total 100%, and are plotted as abscissæ on rectangular co-ordinates, whilst the ordinates give $CaO : (MgO + FeO + MnO)$. The dots representing the several analyses fall into more or less well-defined areas on these diagrams, and from them the following conclusions are drawn. There is a continuous series of mixed crystals between Fe-Al-garnet (almandine) and Mg-Al-garnet (pyrope), and also between almandine and Mn-Al-garnet (spessartite); but between pyrope and spessartite there is a very wide gap. Between the lime-garnets and those just mentioned there is a break in the series from 20 to 75% (Mg,Fe,Mn)O. Between Ca-Al-garnet (grossularite) and Ca-Fe-garnet (andradite) there is a continuous series. In pyrope, almandine, and spessartite, alumina can be replaced isomorphously by ferric oxide only up to the extent of 45%; and with increasing ferric iron there is correspondingly less calcium present.

L. J. S.

Analytical Chemistry.

The Application of the Ionic Theory in Analytical Chemistry. O. HACKL (*Jahrb. K. K. Geol. Reichsanstalt*, 1913, **62**, 613—648).—A criticism of a statement by W. Ostwald ("Die wissenschaftlichen Grundlagen der Analytischen Chemie") on this subject.

F. M. G. M.

Burette with Automatic Setting of the Zero Point. P. HAERTL (*Zeitsch. anal. Chem.*, 1913, **52**, 759—760).—An improved automatic burette, which can be affixed to any bottle filled with stock liquid, is described and figured.

L. DE K.

A New Still-head with Dropping Funnel. OTTO RAMMSTEDT (*Zeitsch. angew. Chem.*, 1913, **26**, 640).—For estimations which involve the addition of a reagent immediately preceding or during a distillation, a device is described in which a graduated dropping funnel is fused to the stem of a still-head of the type commonly used for ammonia distillations.

J. C. W.

New Apparatus for the Rapid Estimation of Water in Foods and Fodder. ARTUR FORNET (*Chem. Zeit.*, 1913, **37**, 1400).—The author has carried out a series of determinations of the water content of flour and bran (1) at 100°, (2) at 105°, (3) in a vacuum, and (4) at 125°. The results show considerable variation among themselves. After fourteen to sixteen hours, a further loss of water does not appear to occur, but, on continuing desiccation at 125°, the products treated according to (1) and (2) were further dehydrated, the loss ultimately attaining the same value as in (3) or (4). The author is therefore led to the conclusion that the generally adopted methods of determining moisture in grain, bran, and flour yield too low results. The latter are, however, satisfactory if heating takes place during four hours at 105° in a stream of air.

The author has further investigated the possibility of desiccation at a higher temperature; this is found to be complete in about ten minutes at 180°, and can be effected without decomposition of the substance provided that the duration of heating, determined for any class of substance by comparison of the loss obtained by this method with the analytically determined amount of moisture, is not exceeded. The necessary apparatus consists of a drying oven which can be rapidly heated to and easily maintained at 160°, and a lever arrangement by which the substance can be weighed whilst hot, and which is so calibrated that the percentage of moisture can be read directly.

The author replies to some criticisms by Parow (*Chem. Zeit.*, 1913, **37**, 345), who, using the above method, found too low values for the percentage moisture in starch. The explanation is to be

found in the fact that the method yields only conventional results, and therefore, if standardised against starch at 105°, naturally yields results which are low when compared with the loss observed at 120° if the duration of heating is kept constant. H. W.

The Estimation of Traces of Chlorides in Water. MAURICE LOMBARD (*Bull. Soc. chim.*, 1913, [iv], 13, 1006—1011).—In estimating traces of chlorides in natural waters by titration with $N/100$-silver nitrate solution, using potassium chromate as an indicator, it is necessary to take certain precautions. A known volume of the water (150—200 c.c.) must be boiled until all the calcium hydrogen carbonate is decomposed, then it is allowed to cool, made up to the original volume, left to settle, decanted, and 100 c.c. of the clear liquid titrated with the silver nitrate. The eud-point is determined by colorimetric test against the end-point made with 100 c.c. of a standard solution containing 5 mg. of sodium chloride per litre. Hydrogen sulphide in water is destroyed by boiling with a slight excess of nitric acid, which is finally removed by the addition of calcium carbonate. Ammonia can be similarly neutralised. W. G.

Estimation of Periodate in Presence of Iodate and Iodide ERICH MÜLLER and GUSTAV WEGELIN (*Zeitsch. anal. Chem.*, 1913, 52 755—759).—To 20 c.c. of the solution (about $N/10$-strength) are added 20 c.c. of a saturated solution of borax containing 0·5 gram of free boric acid, 2 grams of potassium iodide are added, and the liberated iodine, which represents one-quarter of the periodate oxygen, is titrated with $N/10$-arsenious acid. Dilute sulphuric acid is now added until the liquid is acid to Congo-paper, and after again neutralising by means of a saturated solution of borax, the iodine liberated is again titrated. If in the first titration a c.c. of $N/10$-arsenic were used, and b c.c. in the second, $4a$ c.c will represent the periodate, and $a+b-4a=b-3a$ the iodate oxygen. L. DE K.

Estimation of Fluorine in Zinc Ores. LEOPOLD SCHNEIDER (*Österr. Zeitsch. Berg. Hüttenwesen*, 1913, 16, 365—367).—The estimation of fluorine in minerals by distilling with concentrated sulphuric acid over quartz and weighing the orthosilicic acid ($Si(OH)_4$) subsequently separated by means of water (Bein, A., 1888, 527) is considered unsatisfactory; aud a method is now described in which the fluorine is precipitated and weighed as calcium fluoride in the presence of silica, and the latter afterwards removed by treatment with hydrofluoric acid. F. M. G. M.

A Simple Method of Calibrating the Differential Blood gas Apparatus. PAUL HOFFMANN (*J. Physiol.*, 1913, 47. 272—274).—A simpler method than that of Barcroft is described, and gives equally good results. W. D. H.

Determination of Alkali Sulphides. DOUGLAS MCCANDLISH and JOHN ARTHUR WILSON (*Collegium*, 1913, 80—84).—A discussion

of the method advocated by Blockey and Mehd (A., 1912, ii, 600) for the estimation of sulphur in lime liquors, with a description of modifications which are considered to give more satisfactory results.

F. M. G. M.

Source of Error in Estimating Nitrogen in Urine by Kjeldahl's Method. O. von Spindler (*Chem. Zentr.*, 1913, ii, 1340; from *Schweiz. Woch. Chem. Pharm.*, 1913, **51**, 517—521).—Under ordinary conditions of feeding, urine almost always contains nitrates, and their presence affects the results in the estimation of the total nitrogen in the urine by Kjeldahl's method. Loss of free nitrogen takes place, but is not proportional to the quantity of nitrate present. The loss may be diminished by taking care that not more than 0·01 gram of nitric acid is present in the quantity of urine used for the estimation, and that the volume of the digestion mixture is not too small at the commencement of the operation.

W. P. S.

Decomposition of Organic Substances by Kjeldahl's Method and the Estimation of Nitrogen in Barley. Kurt Bunge (*Pharm. Zentr.-h.*, 1913, **54**, 1127—1128).—The following procedure is recommended, as it allows a relatively large quantity of the sample to be taken for the estimation. Ten grams of the unground barley grains are heated for thirty minutes with 60 c.c. of sulphuric acid, and about 1·5 grams of mercury in a round-bottom, 500 c.c. flask. To the dark-coloured solution are then added 25 grams of potassium sulphate, and the heating is continued until a clear solution is obtained; the solution is now cooled, diluted to 500 c.c. with water, and the ammonia is estimated in an aliquot portion.

W. P. S.

Ammonia Absorption Apparatus for Nitrogen Estimations. Herbert Lickfett (*Zeitsch. angew. Chem.*, 1913, **26**, 688).—The absorption flask has a wide neck, and is fitted with a rubber stopper, through which pass (1) the tube from the condenser and (2) a tube with two glass bulbs; this tube may be adjusted, so that the end just dips below the surface of the standard acid in the flask.

W. H. G.

Detection of Nitric Acid (Nitrates) in Milk. R. Barth (*Zeitsch. Nahr. Genussm.*, 1913, **26**, 339—341).—The formaldehyde-sulphuric acid test is recommended. Ten c.c. of the milk are mixed with 5 drops of dilute formaldehyde solution (10 drops of 40% formaldehyde in 250 c.c. of water), and the mixture is poured on the surface of 5 c.c. of sulphuric acid, D 1·71, contained in a test-tube. A blue ring appears at the junction of the two liquids when the milk contains not less than 0·5 mg. of nitric acid per litre. Care must be taken to see that the sulphuric acid, water, etc., used in the test are free from nitric acid.

W. P. S.

Estimation of Phosphorus in Fertilisers and Fodders. C. Dusserre and P. Chavan (*Chem. Zentr.*, 1913, ii, 1333—1334; from *Mitt. Lebensmittelunters. Hyg.*, 1913, **4**, 261—267).—Molinari's

modification of Pemberton's method, in which Petermann's solution is added to the phosphate solution, yields trustworthy results in the case of superphosphates, but the results are too low with Thomas slag and bone-meal when sulphuric acid solutions of these substances are used for the estimation. This error may be avoided by adding ammonium sulphate to the molybdic acid reagent in place of the usual ammonium nitrate. The molybdic acid reagent is prepared by adding a solution of 25 grams of ammonium sulphate in 400 c.c. of nitric acid, D 1·12, to 75 grams of ammonium molybdate dissolved in 500 c.c. of water, aud diluting the mixture to 1 litre. Results of analyses are given showing the distribution of phosphorus in hay (as lecithin, inorganic, and nuclein compounds). The lecithin-phosphoric acid was estimated by extracting the hay repeatedly with boiling alcohol, then with ether, evaporating the solutions, and oxidising the residues with a mixture of sulphuric and nitric acids. The hay was next extracted with cold 1% hydrochloric acid to obtain the inorganic phosphates in solution, and the nuclein-phosphoric acid was estimated by digesting the hay subsequently with sulphuric and nitric acids; in all these estimations, the phosphoric was, finally, precipitated with molybdic acid reagent. W. P. S.

Source of Error in the Precipitation of Ammonium Magnesium Phosphate in the Presence of Ammonium Citrate. ALFREDO QUARTAROLI (*Chem. Zentr.*, 1913, ii, 539; from *Staz. sperim. agrar. ital.*, 1913, **46**, 322—328).—Results of experiments are given in tabular form showing that the amount of phosphoric anhydride, precipitated as ammonium magnesium phosphate in the presence of ammonium citrate, diminishes rapidly as the quantities of ferric and aluminium compounds in the solution increase. W. P. S.

Reactions of Boric Acid and Methyl Alcohol. ERNST PIESZCZEK (*Pharm. Zeit.*, 1913, **58**, 850—851).—A mixture of borax and methyl alcohol yields a green-coloured flame when ignited, and the addition of sulphuric acid is unnecessary. Since ethyl alcohol, acetaldehyde, and acetone do not yield a green flame when burnt in the presence of borax unless a mineral acid is also present, the test may be used, conversely, for the detection of methyl alcohol in ethyl alcohol. The presence of 5% of methyl alcohol may be detected by this means. W. P. S.

Titration of Boric Acid. EDMUND B. R. PRIDEAUX (*Zeitsch. anorg. Chem.*, 1913, **83**, 362—368).—A comparison of the behaviour of various indicators with the neutralisation curve of boric acid suggests the possibility of titrating boric acid without the addition of glycerol or mannitol. The neutralisation curve has been determined from the results of Schmidt and Finger (A., 1908, ii, 802) aud Sörensen (A., 1909, i, 861; 1910, i, 147). The best indicator is tropaeolin-O (sodium *p*-benzeneazoresorcinolsulphonate), using 0·5 c.c. of a 0·04% solution for a total volume of about 68 c.c. The

accuracy of the titration in concentrated and dilute solutions, and also with the addition of sodium chloride, is in agreement witb that calculated theoretically. The method may be used with an accuracy of $\pm 1\%$. C. H. D.

Absorbing Apparatus for the Estimation of Carbon in Organic Analyses. HENRI VIGREUX (*Bull. Soc. chim.*, 1913, [iv], 13, 955—958).—The gas produced in the combustion passes through a straight tube to the bottom of the first washer, where it passes into an outer tube, the inner surface of which is spirally furrowed. The gas passes along the furrow, and escapes by a minute hole at the top leading into the second washer, which is of the usual pear-shaped bubble-counter pattern. The progress of the combustion can be watched easily by comparing the sizes of the bubbles of gas in the two washers. A modified form of the apparatus is also made for the estimation of iodine or chlorine, or of oxidising agents liberating chlorine by the action of hydrochloric acid. Figures are provided in the original. T. A. H.

Tube for the Absorption of Water in Elementary Analysis. JEAN NIVIÈRE (*Bull. Soc. chim.*, 1913, [iv], **13**, 958—959).—The apparatus which is figured in the original consists of a tube closed at the bottom and having a constriction about one-quarter of its length from the bottom, and two narrow side-arms near the top. The side-arm used as an inlet is prolonged inside to the bottom of the tube. The latter is filled nearly to the constriction with sulphuric acid, and above that with pumice stone previously soaked in sulphuric acid. T. A. H.

Apparatus for the Extraction of Carbon Monoxide from Blood. MAURICE NICLOUX (*Bull. Soc. chim.*, 1913, [iv], **13**, 947—952).—The apparatus consists essentially of a long-necked flask, the neck of which is jacketed to carry a current of cold water. The mouth of the flask is closed by a hollow ground glass stopper carrying a T-piece of special form, the two outer limbs of which are provided with stoppers, and terminate in funnels of special form, by means of which the flask can be (*a*) exhausted, and (*b*) supplied with the blood under examination. The blood is run into dilute phosphoric acid in the flask, and the gas liberated can, by appropriate manipulation, be collected and withdrawn for examination. The apparatus is figured in the original, and results obtained by its use are quoted. T. A. H.

Application of the Electrical Conductivity to the Investigation of Natural Waters. ANTONY G. DOROSCHEVSKI and S. V. DVORSHANTSCHIK (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1489—1528).—The authors havo investigated the relation of the electrical conductivity to the amount of dry residue in the case of a number of salt solutions and of natural waters. With salt solutions, especially those of calcium and, to a greater extent, magnesium salts, drying of the residue for two hours at 110° gives

results very considerably in excess of the true values, owing to the retention of water of crystallisation. When, however, the water is evaporated, together with a definite proportion of standard sodium carbonate solution sufficient to convert the calcium and magnesium salts into carbonates, the corrected experimental results never exceed the actual values by more than 1—2%; at the same time, almost identical results are then obtained at 110° and 103°. With artificial mixed salt solutions resembling natural waters in composition, similar results are obtained, drying at 103° in presence of excess of sodium carbonate giving numbers 0·51—2·19% in excess, whilst at 110° the divergence varies from 0·29% to 1·69%; in general, the difference between the values obtained at 103° and at 110° does not exceed 0·5%, and the use of the lower temperature is recommended, since decomposition of the organic matter and of certain of the inorganic salts present is thereby restricted.

Investigation has also been made, with solutions containing a single salt and with others resembling natural waters in composition, of the variation with the concentration of the magnitude of the coefficient $C = M/\kappa . 10^6$, where M represents the number of milligrams of salt present per litre, and κ the specific conductivity in reciprocal ohms at 18°. With sodium and potassium salts and with calcium chloride, C increases gradually with the concentration, but with calcium and magnesium sulphates the increase is decidedly more rapid, so that the selection of a mean value of C is possible only within very narrow limits of concentration. Since the great majority of natural waters contain 0·2—0·3 gram of solids per litre, all waters should be diluted to this concentration with pure distilled water before their conductivities are measured. For a number of mixed salt solutions of such concentrations and having compositions such as are met with in natural waters, the mean value of C is found to be 0·668. The formula for calculating the amount of dry residue from the conductivity then assumes the form: $M = \kappa_x . 10^6 . x . C$, where M represents the residue in milligrams per litre obtained by evaporating with sodium carbonate and drying at 103°, x is the extent to which the water is diluted, and κ_x is the conductivity at a dilution corresponding with 0·003—0·004 gram-equivalent per litre, for which $\kappa_{18} . 10^6$ has the value 300—400 at 18°.

With natural waters of different types, the value of C varies very considerably, more particularly with the permanent hardness (magnesium and calcium sulphates) and with the chlorine; the authors recommend that, in calculating the dry residue of a water from its conductivity, the value of C taken should be as follows: For a soft water with a high chlorine-content (more than 50 mg. per litre), 0·670; for a hard water containing little chlorine (less than 20), 0·725; and for all other waters, 0·695. In all cases air should be bubbled through the water for an hour prior to the measurement of the conductivity.

Frequent measurements of the conductivity were made during the seven months, October—April, for an artesian well water and for the Moscow water-supply, which is of river origin. With the

former, the value of $\kappa_{18}.10^6$ varied only from 602·0 to 609·3, whilst with the river water the conductivity showed a decided fall in October, as a result of heavy rainfall, and an enormous fall in March, owing to the introduction of large volumes of ice- and snow-water into the river; in this case the limiting values of $\kappa_{18}.10^6$ were 124·5 and 450·8. It is evident that systematic measurement of the conductivity furnishes a valuable means of controlling the composition of a water-supply.

The results of preliminary experiments indicate that conductivity measurements may also serve for the estimation of the permanent and temporary hardness of a water. The hardness, in German degrees, is expressed by the following empirical formula:

$$H = H_t + H_p = (\kappa_n + \kappa_k)/A_t + y\{(\kappa_k + \kappa_c - x_p - \kappa_0)/A_p + 1\},$$

where H_t and H_p represent respectively the temporary and permanent hardness, κ_n the conductivity of the original water, κ_k that after boiling for an hour, κ_c that of a solution of sodium carbonate containing 0·01 gram-equivalent per litre, κ_0 that of the water after treatment with sodium carbonate, x_p the corresponding correction for change of concentration, y the extent to which the water is diluted before its conductivity is measured, and A_t and A_p the magnitudes of the conductivity corresponding with 1 degree of temporary and permanent hardness respectively. The value of A_t for river water is 25, and for artesian well water, 22, whilst the value of A_p varies with $(\kappa_k^1 + \kappa_c - x_p)$ from 23 to 25. Application of this method to various river and well waters gives results in moderately good agreement with those obtained directly.

T. H. P.

Hydrolytic Reactions which Take Place During the Estimation of the Total Solids in Waters. P. KACHINSKI (*Ann. Chim. anal.*, 1913, 18, 385—389).—During the evaporation of saline solutions containing magnesium salts, hydrolysis of the latter occurs, and loss of chlorine, bromine, and iodine takes place. This loss is accentuated when the dry residue is incinerated, and, as regards the chlorides, may amount to about 50% of the total chlorine present.

W. P. S.

Estimation of Hardness in Water by Blacher's Method. WALTER PFLANZ (*Chem. Zentr.*, 1913, ii, 1164—1165; from *Mitt. K. Landesanst. Wasserhyg.*, 1913, 141—148. Compare this vol., ii, 153, 518).—Dimethylaminoazobenzene possesses no advantage over methyl-orange as an indicator in this method; even in the case of waters containing humic substances, methyl-orange may be used, provided that the water is titrated with $N/10$-acid until distinctly acid towards this indicator, and the excess of acid then titrated with $N/10$-alkali, using phenolphthalein as indicator. It is essential that the potassium palmitate solution employed in the process should be free from stearic acid.

W. P. S.

Volatility of Sodium Chloride in Presence of Potassium Chloride. M. WAGENAAR (*Pharm. Weekblad*, 1913, 50, 1214—1215).—In estimating the alkali metals in potable waters there is no

danger of altering the relative proportions of the chlorides of sodium and potassium by igniting the chloride mixture.

A. J. W.

Estimation of the Alkali Hydrogen Carbonate Content of Natural Waters. PIETER A. MEERBURG (*Chem. Weekblad*, 1913, 10, 958—959).—The amount of alkali hydrogen carbonate in natural waters can be estimated by evaporation of 1—3 litres to small bulk, filtration, titration of the alkali hydrogen carbonate in the filtrate with $N/10$-hydrochloric acid and methyl-orange, and estimation of the magnesium. A simpler method involves the estimation of the alkali and the determination of the hardness, but the results of the two methods do not always agree. A. J. W.

The Estimation of Calcium Oxide Mixed with Calcium Hydroxide. GEORG WEISSENBERGER (*Österr. Chem. Zeit.*, 1913, [2], 16, 192—193).—A discussion of the errors resulting from the method of estimating calcium by means of its combined constituents, such as the amount of water evolved by calcium hydroxide or the quantity of calcium carbonate obtained from calcium oxide; this untrustworthiness is demonstrated by the analysis of mixtures containing known proportions of calcium oxide and hydroxide. F. M. G. M.

Estimation of Calcium as Oxalate. SAMUEL GOY (*Chem. Zeit.* 1913, 37, 1337—1338).—Calcium may be conveniently estimated as hydrated calcium oxalate, but in order to obtain correct results the following conditions should be observed.

The calcium should be precipitated by ammonium oxalate at the boiling heat, and the oxalate collected in a Gooch crucible in connexion with a suction apparatus. After washing the precipitate with small quantities of water until free from ammonium oxalate, the crucible and contents are dried for four to five hours at exactly 105°. The dried compound has the composition CaC_2O_4,H_2O. Drying on a filter gives erroneous results.

L. DE K.

Detection of the Metals of the Alkaline Earths by Spectrum Analysis in the Course of Qualitative Analysis. II. ERNST H. RIESENFELD and G. PFÜTZER (*Ber.*, 1913, 46, 3140—3144. Compare A., 1906, ii, 804).—An apparatus for the production of an arc spectrum between an iridium electrode and a small quantity of a solution is described. The liquid is contained in a 1—2 c.c. glass tube, through the bottom of which a platinum lead is fused. The electrode may be raised or lowered over the liquid by means of a micrometer screw, and other screws facilitate the adjustment of the whole device before the slit of a spectroscope. The chief magnesium lines may be detected in the arc spectrum in a dilution of 0·1 mg. per c.c., the calcium lines with 0·002 mg. per c.c.; strontium, 0·03 mg. per c.c.; and barium, 0·006 mg. per c.c. Large excesses of the other earths are no drawback to the detection of magnesium. The arc spectra are 20 to 2000 times as sensitive as the flame spectra.

The procedure is not advantageous in the case of potassium, but the sodium line, $568 \cdot 6\mu\mu$, appears with 0·04 mg. of the metal per c.c., and may thus be taken as an indication of the presence of weighable quantities in a solution. J. C. W.

Radio-elements as Indicators in Analytical Chemistry. FRITZ PANETH and GEORG VON HEVESY (*Monatsh.*, 1915, **34** 1401—1407).—The chemical non-separability of lead and radio-lead, or radium-*D*, lends itself to the use of radium-*D* as an indicator for lead in quantities too small to be otherwise estimated. The quantities necessary for detection are 10^{-10} gram of radium-*D* by the β-rays of radium-*E*, and 10^{-12} gram by the α-rays of radium-*F* by waiting until the latter attains equilibrium (a year or more). The radio-lead from pitchblende contains about 10^{-7} gram of radium-*D* per gram, so that about 1 mg. can be detected by the β-ray method. For more sensitive measurements the radium-*D* content must be increased by addition of the products of radium emanation. The products of 0·2 curie were mixed with 10 mg. of lead chloride, potassium chromate was added, and the liquid made up to 100 c.c. was shaken in a thermostat at 25° for twenty-four hours. The activity of the evaporated filtrate was measured after radium-*E* had reached equilibrium by comparing it with that of 1 c.c. of the original solution before precipitation, and corresponded with that of 0·012 mg. of lead chromate per litre. Lead chromate is the least soluble lead salt, the solubility of lead phosphate being of the same order. Similarly the solubility of lead sulphide was found to be in pure water at 25° 0·3 mg. per litre, and in water saturated with hydrogen sulphide 0·15. Similarly, radium-*E* may be used as an indicator for bismuth, and ionium as an indicator for thorium. F. S.

Cathodic Estimation of Lead and Analysis of Lead Alloys. R. GARTENMEISTER (*Chem. Zeit.*, 1913, **37**, 1281—1282).—The author finds that gallic acid is a suitable addition-agent, in the electrolysis of solutions of lead salts, for preventing the deposition of lead dioxide at the anode and the evolution of hydrogen at the cathode. Quantitative deposits of lead on the cathode may be obtained by observing the following conditions. For estimating quantities of lead up to 1 gram, the electrolyte should have a volume of about 125 c.c., and contain 2—2·5 c.c. of nitric acid (D 1·4), 5 grams of gallic acid, and 5—6 c.c. of alcohol. The anode should be a cylinder of platinum foil and be surrounded by a Winkler cylindrical gauze cathode. Using a current of 1·2 amperes, the time of electrolysis (stationary electrodes) is four hours at 65—70° for 1 gram of lead. This time must not be exceeded to any great extent, otherwise a yellow dye is deposited.

Zinc, cadmium, iron, nickel, cobalt, and manganese are not deposited under the above conditions. Silver, tin, arsenic, and antimony form black, rough deposits. Bismuth is precipitated as bismuth gallate, and does not interfere. Copper is deposited with the lead.

Alloys of lead, tin, and antimony are best analysed as follows. One to two grams of the alloy are dissolved in a mixture of nitric and tartaric or citric acids. The solution is made alkaline with sodium hydroxide, and then precipitated with sodium sulphide. The lead sulphide is collected, washed with sodium sulphide solution, and finally with a strong solution of ammonium chloride containing some ammonium hydroxide and ammonium sulphide. The lead sulphide, which may also contain copper, iron, and zinc sulphides, is dissolved in nitric acid, the solution filtered, the filter paper ashed, and the ash dissolved in nitric acid and added to the solution, which is then evaporated to dryness. The residue is taken up with nitric acid, and the lead estimated as above. The weight of the deposit has to be corrected for copper, which is estimated separately. The antimony and tin in the filtrate from the lead sulphide are estimated electrolytically in the usual way. T. S. P.

Detection of Lead in Bismuth Subnitrate and Bismuth Carbonate. Gabriel Guérin (*J. Pharm. Chim.*, 1913, [vii], 8, 422—424).—The test depends on the insolubility of bismuth subnitrate in ammonium nitrate solution, whilst lead sulphate, carbonate, etc., are soluble. Further, bismuth carbonate is converted into bismuth subnitrate when boiled with ammonium nitrate solution. For the detection of lead in bismuth subnitrate, 10 grams of the sample are boiled for three minutes with 50 c.c. of 5% ammonium nitrate solution; the mixture is then cooled, filtered, and the filtrate is tested with potassium chromate solution; the test will detect the presence of 1 mg. of lead in 10 grams of the subnitrate. In the case of bismuth carbonate, 10 grams are heated to boiling with 100 c.c. of 5% ammonium nitrate solution, the mixture is evaporated to dryness, 100 c.c. of water are added to the residue, and evaporated to a volume of about 40 c.c. It is essential to expel completely the ammonium carbonate resulting from the reaction. When cold, the mixture is filtered, and the filtrate tested as described. W. P. S

Estimation and Detection of Lead in Organic Materials and the Separation of Lead and Calcium Sulphates by Ammonium Acetate. Ernst Erlenmayer (*Biochem. Zeitsch.*, 1913, 56, 330—340).—The organic material is incinerated, and the ash is digested with 20% sodium carbonate. The insoluble residue is then digested with 5*N*-nitric acid, and the greater part of the lead is dissolved. The insoluble residue still contains lead, and is fused with sodium and potassium carbonate mixture. The fusion is then extracted with 5% sodium carbonate, the insoluble residue containing the lead is extracted with nitric acid, and this extract is added to the nitric acid solution containing the main bulk of the lead. The solution of lead in nitric acid is evaporated on a water-bath, the residue is extracted with water, ammonia is added until alkaline reaction, then acetic acid until acid reaction, and the mixture is then digested for two hours. The aluminium and iron and the greater part of the calcium remain undissolved, and in the filtrate from these the lead is precipitated by the addition of ammonium

dichromate added as powder. The lead chromate is then converted into the sulphate and weighed as such. For qualitative analysis the ash is extracted with nitric acid, the lead is precipitated as sulphate by addition of sulphuric acid and concentration, and the precipitate, after washing with 4% sulphuric acid, is treated with hydrogen sulphide, the formation of the black sulphide indicating the presence of lead. Lead and calcium sulphates can be separated by treating them with a mixture of equal volumes of alcohol and concentrated ammonium acetate, in which the lead sulphate is much more readily soluble. S. B. S.

[Estimation of Copper. Iodometric Estimation of Iron.] CHR. BECK (*Chem. Zeit.*, 1913, **37**, 1330—1331).—*Estimation of Copper as Cuprous Sulphide.*—The usual method (ignition of copper sulphide + sulphur in a Rose's crucible) is employed, with this difference, however, that instead of a current of hydrogen or hydrogen sulphide, a current of carbon dioxide is used. The crucible should be heated over a full Bunsen flame.

Iodometric Estimation of Iron.—The iron which should be present in the ferric state is distilled in a suitable apparatus with dilute hydrochloric acid (1 : 2) and about 2 grams of potassium iodide, with addition of a few lumps of marble to generate an atmosphere of carbon dioxide. The iodine liberated is distilled off and collected in a suitable receiver containing 2 grams of potassium iodide dissolved in 100 c.c. of water; the receiver should be cooled by ice-water. When the bulk of the liquid has passed over, the receiver is at once disconnected (before turning off the gas) and the contents titrated with sodium thiosulphate. L. DE K.

Analysis of Alloys Containing Copper, Nickel, and Zinc [German Silver, Alpaka, etc.]. CHARLES LIND (*Chem. Zeit.*, 1913, 37, 1372).—The alloy (0·5 gram) is dissolved in concentrated nitric acid (10 c.c.). The solution is boiled, diluted with water (50 c.c.), and rendered alkaline by addition of concentrated ammonia solution. Excess of ammonia is removed by nitric acid (D 1·18), a further 3 c.c. of this acid are added, the solution diluted to 100 c.c., heated to boiling, and the copper determined electrolytically. Deposition is complete in fifty minutes when rotating platinum gauze electrodes are used, the current being 3 amperes and potential difference 3 volts.

For the estimation of zinc, the residual solution is neutralised with ammonia, acidified by two drops of nitric acid (D 1·18), heated to about 50°, and treated with hydrogen sulphide for an hour. The precipitated zinc sulphide is collected, washed with a solution of ammonium chloride (2 grams in 100 grams of water), and dissolved in dilute sulphuric acid. After treatment with potassium hydroxide (10 grams), the solution is diluted to 100 c.c., and the zinc deposited electrolytically on the coppered platinum gauze electrodes (obtained above). The current employed is 0·8—1 ampere, the potential difference 4 volts. With rotating electrodes, 0·1 gram of zinc is quantitatively deposited in sixty minutes.

Nickel is determined in the filtrate from the zinc sulphide by the dimethylglyoxime method.

The process is accurate, and can be carried out in a comparatively short time. It has the further advantage that small quantities of impurities, such as tin, lead, iron, and manganese, can be simultaneously estimated. H. W.

Estimation of Free Acid and Basicity of Aluminium Sulphate. W. N. IVANOV (*Chem. Zeit.*, 1913, **37**, 805—806).—The methods of estimating free acid, or, in its absence, the basicity of aluminium sulphate, may be divided into three groups depending on: (1) direct titration with various indicators; (2) precipitation of aluminium hydroxide by magnesium ammonium phosphate and titration of the acid in the filtrate; and (3) Beilstein and Grosset's method (A., 1890, 85), in which the substance is dissolved in water, treated with saturated ammonium sulphate solution, and finally with alcohol. The precipitate is filtered and washed with alcohol, the alcoholic filtrate being evaporated, the residue dissolved in water, and titrated with $N/2$-sodium hydroxide in the presence of methyl-orange. The first two methods gave unsatisfactory results. The third method is also found to be untrustworthy, since the amount of free acid found depends on the quantity of water and alcohol used, and can amount to the sum of free and combined acid actually present. Under the usual analytical conditions, a content of 0·25% free acid can easily be found in a preparation which actually has a 90% basicity. H. W.

Electrolytic Reduction of Iron for Analysis. J. CLYDE HOSTETTER (*J. Washington Acad. Sci.*, 1913, **3**, 429—432).—The following method is proposed for the reduction of ferric sulphate for subsequent titration with permanganate. The ferric sulphate solution, measuring about 300 c.c., is placed in a gold basin, and 10 c.c. of sulphuric acid, D 1·84, are added; a porous cell is now placed in the solution, and filled with dilute sulphuric acid (1 : 30). A piece of platinum foil (area 28 sq. cm.) is inserted in the porous cell, and serves as the anode, whilst the gold basin acts as the cathode. A current of about 8 amperes is passed through the solution for seventy minutes (0·5 gram of iron is reduced to the ferrous condition in this time), the contents of the anode chamber are then transferred to the basin, the chamber is refilled with dilute acid, and the electrolysis is continued for a further ten minutes. The solution in the basin is then titrated with permanganate solution. Before the titration, a drop of the solution may be tested with thiocyanate to ascertain whether the reduction has been completed. W. P. S.

Analysis of Commercial Nickel. L. BERTIAUX (*Ann. Chim. anal.*, 1913, **18**, 377—385).—Methods are given for the estimation of such impurities as copper, cobalt, iron, manganese, aluminium, calcium, magnesium, sulphur, silicon, carbon, arsenic, and antimony in commercial nickel. The following is an outline of the procedure

recommended. The metal is dissolved in a mixture of hydrochloric and sulphuric acids, the solution is rendered ammoniacal, and the nickel, cobalt, and copper are deposited electrolytically. The deposit consisting of the three metals is then dissolved in nitric acid, the copper is deposited from this solution, the cobalt is precipitated as potassium cobaltinitrite, and the nickel remaining in solution is estimated electrolytically. Iron, manganese, aluminium, calcium, and magnesium are estimated in the solution after the removal of the nickel, cobalt, and copper. Silica and sulphur are estimated in a separate portion of the sample in the usual way. The distillation method is employed for the estimation of the arsenic and antimony, and the carbon is estimated by combustion.

W. P. S.

Titration of Titanium by means of Methylene-blue. BERNHARD NEUMANN and ROBERT K. MURPHY (*Zeitsch. angew. Chem.* 1913, **26**, 613—616).—The authors have investigated and confirm the accuracy of Knecht and Hibbert's method of titrating titanium with methylene-blue (compare Knecht, A., 1907, ii, 654; Hibbert, A., 1909, ii, 351). The reaction proceeds according to the equation: $C_{16}H_{18}N_3ClS + 2TiCl_3 + HCl = C_{16}H_{18}N_3S + 2TiCl_4$, and is exactly molecular, but, owing to the difficulty of obtaining the pure dye, the solution employed must be standardised. Best results are obtained with 0·02—0·04*N*-solutions, made by dissolving 3·9 to 7·8 grams of the dye in hydrochloric acid and filtering into dark glass bottles. The controlling solution is made from Merck's 15% solution of titanous chloride, in which case titanium is first separated from the accompanying ferrous chloride and estimated by gravimetric methods, or pure titanic oxide may be prepared from titanic acid, which usually contains silica and oxides of iron and aluminium, by the method of Bornemann and Schirmeister (A., 1910, ii, 1073). The strongly acid solution of titanium chloride is then reduced by zinc dust and filtered into a flask, which is fitted with an inlet tube and a Bunsen valve. To complete the reduction, a clean zinc rod is suspended in the liquid, and this is kept nearly boiling, whilst a stream of carbon dioxide is admitted. The zinc rod is then removed, the burette is inserted into the valve, and the methylene-blue solution is run in until the blue colour is permanent. The bulk of the liquid should be about 150 c.c. (compare Hibbert, *loc. cit.*).

For the estimation of titanium, the substance is fused with sodium hydroxide and sodium peroxide, and then dissolved in concentrated hydrochloric acid. If sulphuric or nitric acid is used to dissolve the sample, the titanium must be precipitated by ammonia and re-dissolved in hydrochloric acid. The reduction and titration are then carried out as above, the process requiring about forty-five minutes after the fusion. Iron, even in overwhelming proportion, aluminium, silicon, calcium, alkalis, magnesium, zinc, antimony, arsenic, and phosphorus do not influence the titration, but salts of the lower oxides of tin, vanadium, or tungsten, and also sulphurous acid, must not be present.

The method is useful when mere traces of titanium are present, is more accurate than the known methods (a critical review of which is given), and is the only one which permits of the direct estimation of titanium in presence of iron, silica, or alumina. J. C. W.

Assay of Platinum Ores. MAX WUNDER and V. THÜRINGER (*Zeitsch. anal. Chem.*, 1913, 52, 740—752).—The process is practically the old one of Saint-Claire Deville and Debray incorporated with the authors' new processes for the estimation of palladium. L. DE K.

Estimation of Palladium with Nitroso-β-naphthol in Presence of Copper and Iron. MAX WUNDER and V. THÜRINGER (*Zeitsch. anal. Chem.*, 1913, 52, 737—739).—The solution containing about 0·25 gram of palladium and small quantities of copper and ferric iron, all present as chlorides, is diluted to about 150 c.c., 20 c.c. of strong hydrochloric and 20 c.c. of glacial acetic acid are added, and then, after heating to boiling, a hot solution of nitroso-β-naphthol in 50% acetic acid is added in excess. On prolonged boiling, a voluminous Kermes-coloured precipitate collects on the surface, which is at once collected on a filter and washed, first with hot 5% hydrochloric acid, and then with hot water. It is then converted into metallic palladium by igniting the filter and contents, first in the air and then in a current of hydrogen; the metal is allowed to cool in a current of carbon dioxide.

The filtrate is nearly neutralised with ammonia, and the copper precipitated as cuprous thiocyanate in presence of sulphurous acid, and weighed as such. The filtrate, after boiling with a little nitric acid, is treated for iron as usual. L. DE K.

Observations of the Abel Heat Test. B. JAMES SMART (*J. Soc. Chem. Ind.*, 1913, 32, 967).—The author discusses and criticises a recent paper by Egerton (this vol., ii, 534). W. P. S.

The Tailameter: A Simple Apparatus for the Rapid Estimation of Volatile Oils in Aromatic Plants, Drugs, and Spices. PROBODHA C. CHATTOPADHYAY (*J. Soc. Chem. Ind.*, 1913, 32, 968).—The apparatus consists of a 500 c.c. flask, the neck of which is graduated into 10 c.c. in one-tenth divisions; a "swan-neck," provided with a tap, is fused into the lower portion of the flask. The distillate obtained on steam-distilling a material containing volatile oils is collected in this flask, and at the end of the distillation, the oil on the surface of the water is brought into the graduated portion of the neck by the addition of more water, and its volume is ascertained. W. P. S.

Simultaneous Estimation of Methyl Alcohol and Formaldehyde in Small Quantities in the Same Solution. MAURICE NICLOUX (*Bull. Soc. chim.*, 1913, [iv], 13, 935—939).—The author has described previously (A., 1899, ii, 253) methods for the estimation of methyl alcohol and formaldehyde separately. The method now described is suitable for both substances in the same

solution, and depends on (1) the estimation of the quantity of potassium dichromate required for complete oxidation of both substances; and (2) the determination of the amount of carbon dioxide produced in the reaction. Exact details of the methods of working and of the calculations required are given. T. A. H.

Estimation of Small Quantities of Methyl and Ethyl Alcohols in Aqueous Solutions of the Same. JÓSEF HETPER (*Zeitsch. Nahr. Genussm.*, 1913, **26**, 342—348).—The method proposed depends on the oxidation of the alcohols by permanganate in acid and in alkaline solution, and is applicable to solutions containing from 0·1 to 0·25% by weight of the two alcohols. Formulæ are given for calculating the quantities of the two alcohols present from the amount of permanganate consumed in the two oxidations (see also this vol., ii, 158). W. P. S.

Methods for Testing Ether. GEORG FRERICHS (*Chem. Zentr.*, 1913, ii, 1254—1255; from *Apoth. Zeit.*, 1913, **28**, 628—630).—Ether which has been prepared from alcohol denatured with wood-spirit and pyridine will contain methyl ethyl ether and acetone; the pyridine remains in the sulphuric acid. Pure ethyl ether has b. p. 34·2—34·3°/1760 mm.; this constant is affected by the presence of methyl ethyl ether, and is raised by 0·2° for each 1% of alcohol which may be present. The boiling point of ether should be determined under a reflux, and a piece of apparatus for this purpose is described. Acetone may be detected in ether by shaking 100 c.c. of the sample with 10 c.c. of water, separating the aqueous layer, and submitting portions of it to the iodoform and sodium nitroprusside tests. W. P. S.

Testing Amyl Acetate. A. HÄMMELMANN (*Chem. Zentr.*, 1913, ii, 1335; from *Farbenzeit.*, 1913, **18**, 2594—2595).—Wolff's method of testing amyl alcohol or amyl acetate for the presence of benzene, based on the solubility of the sample in sulphuric acid, D 1·80, is untrustworthy, since pure amyl alcohol or acetate may yield insoluble alkylene compounds under the conditions of the test. W. P. S.

Testing Amyl Acetate. H. WOLFF and B. ROSUMOFF (*Chem. Zentr.*, 1913, ii, 1335; from *Farbenzeit.*, 1913, **18**, 2641—2642).—Hämmelmann's objection to Wolff's test (see preceding abstract) may be overcome by carrying out the test as follows. The amyl acetate is mixed slowly with 1·5 times its volume of sulphuric acid, D 1·80, the mixture being kept cold and not shaken violently during the operation. When less than 5% of benzene is present, the mixture remains quite clear. W. P. S.

Ignition of Sugar Syrup. M. WAGENAAR (*Pharm. Weekblad*, 1913, **50**, 1213—1214).—In estimating calcium and phosphates in sugar syrup, the sample can be readily ignited to a white ash by transferring it drop by drop to a red-hot platinum dish, the beaker

employed being subsequently weighed to ascertain the weight of syrup taken.
A. J. W.

Estimation of the Sugar in Blood. Walter Griesbach and H. Strassner (*Zeitsch. physiol. Chem.*, 1913, **88**, 199—209).—The blood is first deprived of proteins, preferably by colloidal iron. Estimations of the sugar in the filtrate by the polarimeter and by reduction give the same values for dextrose. After fermentation with yeast, the filtrate exhibits neither reduction nor optical activity. Of the reduction methods used, that of Maquenne and of Bertrand yield almost identical results. Other methods (Bang's, Tachau's, etc.) were also employed. Maquenne's method is recommended on account of its certainty and simplicity. Briefly, it consists in boiling with Fehling's solution, followed after cooling by the addition of potassium iodide and sulphuric acid. Starch is then added, and the free iodine titrated back with thiosulphate.
W. D. H.

Estimation of Hydroxy-fatty Acids in Fat by means of Organic Magnesium Compounds. Th. Zerevitinov (*Zeitsch. anal. Chem.*, 1913, **52**, 729—737).—The total fatty acids are isolated in the usual manner, and carefully dried. About 0·2 gram of the acids is dissolved in pyridine, and to this is then added in a suitable apparatus a solution of magnesium methyl iodide in amyl ether. The gas evolved (methane) is then measured with the usual precautions. 1 mol of methane = 1 mol. of hydroxyl.

If from the result is deducted the carboxyl-hydroxyl, as found by titration with standard alkali in alcohol-ether solution, the difference will be, as the author calls it, the alcohol-hydroxyl number, which represents hydroxy-fatty acid. A large number of results relating to fatty acids and to oils are communicated.
L. de K.

Detection of Citric Acid in Wine, with Reference to a Recent Paper by Fresenius and Grünhut. Georges Denigès (*Ann. Chim. anal.*, 1913, **18**, 393—402. Compare this vol., ii, 255).—The author criticises the statements of Fresenius and Grünhut (*loc. cit.*), maintains the trustworthiness of his method for the detection of citric acid, and shows that it is more sensitive than Möslinger's test. Attention is directed to the experience of other workers with Denigès' method (compare A., 1908, ii, 544, 640, 904).
W. P. S.

Qualitative Detection of Benzoic Acid and Salicylic Acid in Milk and Beer. M. Wagenaar (*Pharm. Weekblad*, 1913, **50**, 1215).—For the estimation of benzoic acid and salicylic acid in milk and beer, the author recommends steam distillation for several hours, neutralisation of the distillate with sodium carbonate, evaporation to small bulk, and the application of the ordinary tests for the acids named.
A. J. W.

Microchemical Detection of Embelic Acid. GEORG HEYL and P. KNEIP (*Chem. Zentr.*, 1913, ii, 1342; from *Apoth. Zeit.*, 1913, 28, 699).—Embelic acid, the active constituent (anthelmintic) of the fruit of the Indian shrub *Embelia ribes*, may be isolated and identified by the micro-sublimation method described by Tunmann. The crystalline sublimate obtained is insoluble in water, but dissolves in dilute sodium hydroxide, yielding a reddish-violet coloured solution; with conceutrated sodium hydroxide solution, violet, crystalline plates separate out after a time, violet needles forming subsequently. These crystals yield a flocculent precipitate of embelic acid when treated with hydrochloric acid. Ammonia also dissolves the sublimate, and on evaporating the solution crystals are obtained. The dilute alkaline solution of the sublimate gives the following reactions: with copper sulphate, an olive-brown precipitate; with barium chloride, a greyish-brown precipitate; with nickel sulphate or cobalt nitrate, a greenish-brown precipitate; with magnesium sulphate, a flocculent, brown precipitate. The colour of the precipitate obtained on treating an alcoholic solution with ferric chloride is reddish-brown; with copper nitrate, dirty green; lead acetate, dark green; and with zinc chloride, violet. Mercuric chloride and silver nitrate yield no precipitate. Whilst pure embelic acid yields a violet coloration when warmed with concentrated sulphuric acid, the sublimate gives but a faint reaction when treated similarly. W. P. S.

The "Chlorine Number," a New Constant of Fats. As. ZLATAROV (*Zeitsch. Nahr. Genussm.*, 1913, 26, 348—349).—A preliminary notice of a method in which it is proposed to estimate the quantity of chlorine fixed by a fat or oil. The fat is treated with saturated solution of phenyliododichloride in carbon tetrachloride, and, after four hours' contact, the excess of the chloride is titrated with silver nitrate solution. W. P. S.

Modified Meig's Method for the Estimation of Fat in Milk. WALTER LEWIS CROLL (*Biochem. Bull.*, 1913, 2, 509—518).—Meig's method is an ether-extraction method. The present paper describes certain proposed modifications which simplify and shorten it, without loss of accuracy. W. D. H.

Detection and Estimation of Minute Quantities of Formaldehyde in the Presence of Hexamethyleneamine, and Methyl Alcohol in the Presence of Ethyl Alcohol. H. A. B. DUNNING (*Amer. J. Pharm.*, 1913, 85, 453—457).—The following test may be used to detect the presence of formaldehyde in the urine of persons who have been given doses of hexamethylenetetramine. About 2 c.c. of the urine are warmed in a test-tube, 2 drops of a 0·5% phenylhydrazine hydrochloride solution are added, followed by 2 drops of a 0·5% sodium nitroprusside solution, and the mixture is then rendered strongly alkaline with sodium hydroxide. One part of formaldehyde in 50,000 parts yields a blue coloration; in more dilute solutions, a green coloration is obtained. Another test

consists in heating the urine with phloroglucinol and then adding sodium hydroxide; when a red coloration develops, formaldehyde is present. The formaldehyde may be estimated colorimetrically by treating 5 c.c. of the urine with 0·1 c.c. of a 15% sodium hydroxide solution, adding 0·1 c.c. of phenylhydrazine (base) and 0·7 gram of sodium hydroxide, and shaking the mixture for ten minutes. The coloration obtained is compared with that produced by similarly treating known quantities of formaldehyde; the comparisons must be made within twenty minutes after the addition of the sodium hydroxide. Dextrose, acetone, and acetaldehyde do not interfere with the estimation.

The method proposed for the detection of methyl alcohol in the presence of ethyl alcohol consists in saturating the mixture of the alcohols with potassium citrate (to remove the greater part of the water), and submitting the mixture to fractional distillation. The low boiling portion of the distillate is then heated in a test-tube, and a hot copper spiral is plunged in the vapour; the characteristic odour of formaldehyde will be noticed if methyl alcohol is present. W. P. S.

Estimation of Paracetaldehyde in Paraldehyde. GEORG HEYL (*Chem. Zentr.*, 1913, ii, 1520; from *Apoth. Zeit.*, 1913, **28**, 720—721. Compare A., 1912, ii, 304).—The method depends on the oxidation of the acetaldehyde to acetic acid by means of hydrogen peroxide in alkaline solution; the excess of the alkali is then titrated. Twenty-five grams of the paracetaldehyde are dissolved in 300 c.c. of cold water, 30 c.c. of $N/1$-potassium hydroxide solution are added, followed by 20 c.c. of 30% hydrogen peroxide solution; the mixture is kept in a closed vessel, and, after eighteen hours, the excess of alkali is titrated, using phenolphthalein as indicator. Each c.c. of $N/1$-alkali solution is equivalent to 0·04403 gram of acetaldehyde. W. P. S.

Detection of Hexamethylenetetramine in Wine and Milk. LEOPOLD ROSENTHALER and E. UNGERER (*Pharm. Zentr.-h*, 1913, **54**, 1153—1155).—Mercuric chloride is the most sensitive reagent for the detection of hexamethylenetetramine; 1 part of the latter in 500,000 parts of solution yields a characteristic crystalline precipitate with the reagent. White wine may be tested directly after the addition of a small quantity of hydrochloric acid, but in the case of red wine it is necessary to treat the sample with solid lead acetate and remove the excess of lead with sodium phosphate before the test is applied. In testing milk, a portion of the sample is treated with hydrochloric acid, saturated with ammonium sulphate, filtered, and the filtrate used for the test. The mercuric chloride precipitate may be further tested by applying to it the morphine sulphuric acid test, or it may be distilled from a sulphuric acid solution, and the resulting formaldehyde identified. W. P. S.

The Gasometric Estimation of Aliphatic Amino-nitrogen in Minute Quantities. DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1913, **16**, 121—124).—By a modification (mainly reduction of size) of

the apparatus previously described (A., 1912, ii, 1008), the author's method is brought within the class of micro-methods, and remains accurate. W. D. H.

Improved Methods in the Gasometric Estimation of Free and Conjugated Amino-acid Nitrogen in the Urine. DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1913, **16**, 125—134).—The author's previously published process (A., 1912, ii, 1008) for estimating total (free and conjugated as hippuric acid, peptides, etc.) amino-acid nitrogen can be simplified, so that the operations are shortened, and the more laborious parts, such as boiling off ammonia and washing milky precipitates, are dispensed with. The free amino-acids alone can readily be estimated after decomposition of the urea with soy-bean urease, which hydrolyses urea completely without either freeing conjugated amino-acids or deaminising free ones. The applicability of the gasometric method for the estimation of hippuric acid is also indicated. W. D. H.

The Separation of *d*-Alanine and *d*-Valine. PHOEBUS A. LEVENE and DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1913, **16**, 103—120).—*d*-Alanine combines with phosphotungstic acid in the approximate ratio 1 : 14 by weight, forming a crystalline salt. At 0° in a solution containing per 100 c.c. 20 grams or more of phosphotungstic acid (in excess of the amount combining with the alanine) and 10 grams of sulphuric acid, the solubility of alanine is only 0·15 gram. The solubility of *d*-valine under the same conditions is 1·21 grams per 100 c.c. By alternate crystallisation of valine as the free amino-acid and of alanine as the phosphotungstate, a practically quantitative separation of the two acids in admixture can be effected. W. D. H.

Estimation of Urea [Carbamide]. H. T. B. RASMUSSEN (*Chem. Zentr.*, 1913, ii, 1335; from *Skand. Arch. Physiol.*, 1913, **30**, 191—195).—The methods proposed by Christensen (*Nord. med. arkiv.*, 1886, 18), and by Henriques and Gammeltoft (A., 1911, ii, 670) were investigated. The former, depending on the hydrolysis of the urea by heating with water under pressure and estimating the resulting carbon dioxide, yields trustworthy results in the case of urea itself, but the results are too high when the method is applied to urine. Henriques and Gammeltoft's method gives lower, and apparently more trustworthy, results. W. P. S.

Estimation of Nicotine in the Form of Silicotungstate. ROSARIO SPALLINO (*Gazzetta*, 1913, **43**, ii, 482—486).—This method gives good results if the product is calcined and weighed in the form of the residue $WO_3 + SiO_2$ so obtained, but not if the silicotungstate is weighed after mere drying at 125°, as has been recommended recently.

Nicotine dipicrolonate, $2C_{10}H_8O_5N_4,C_{10}H_{14}N_2$, forms canary-yellow crystals, m. p. 223°. R. V. S.

New Method of Estimating Nicotine in the Presence of Ammonia. ROSARIO SPALLINO (*Gazzetta*, 1913, **43**, ii, 493—500).—The methods which have been proposed for this purpose do not yield concordant results. The present method depends on the fact that nicotine behaves as a diacidic base towards picric acid in aqueous solution, but in alcoholic solution it behaves as a mono-acidic base. The liquid containing nicotine is treated with an excess of picric acid solution of known strength (0·009 mg. per c.c.). The liquid so obtained is made up to 1 litre with alcohol, and divided into two equal portions, which are then evaporated to dryness. In one case the residue is dissolved in alcohol, and titrated with $N/20$-barium hydroxide. The other is treated with water, made up to 100 c.c., and filtered to remove precipitated picrate; of this solution 75 c.c. are titrated with barium hydroxide as before. No ammonia is lost in the evaporation. The difference between the two titrations (regard being had to the 25 c.c. of aqueous solution not titrated) gives the amount of picric acid present. The method gives accurate results with the solutions of picric acid of known strength in the presence of ammonia, and yields concordant figures in duplicate analyses of ammoniacal distillates from tobacco. R. V. S.

The Triketohydrindene Reaction. CARL NEUBERG (*Biochem. Zeitsch.*, 1913, **56**, 500—506).—A distillate from hexanol gave a positive reaction, and on investigation it was found that substances other than amino-acids gave a positive reaction, which could be distinguished from that given by sugars in alkaline solution recently described by Halle, Loewenstein, and Přibram (this vol., ii, 992). These substances included: I. Amines, which give a direct positive reaction when in combination with weak alkalis. II. Amino-aldehydes, which give a positive reaction when free, or a salt of weak acids. III. Urea derivatives like allantoin, which give the reaction with a pink tinge. IV. Aminosulphonic acids, such as taurine. V. Ammonium salts of aldehyde and keto-acids. VI. Certain organic acids, dicarbonyl compounds, and halogen aldehydes, which have been treated with ammonia in excess, and then freed from this reagent by boiling. The following acids illustrate this reaction: glycollic, lactic, glyceric, malic, and citric acids. Bromal hydrate, phenylglyoxal, and alloxan also give the reaction. The following substances gave a negative or abnormal (colour) reaction: indole, quinoline, *iso*quinoline, cinchonine, brucine, quinidine, morphine, allylthiocarbimide (red), allylamine (yellowish-red), diethylamine (red), piperidine, cyanoacetic acid, thiosinamine, lecithin, betaine, potassium ferrocyanide, choline, camphylamine (red), formamide, amygdalin, diacetonamine, adenine, xanthine, creatine, creatinine, ethyl β-aminocrotonate, trimethylsulphine iodide, aniline, chondroitinsulphuric acid, aminosulphonic acid, barbituric acid, hydrazine, and phenylhydrazine. S. B. S.

Precipitation by Zinc Salts of the Purine Bases from Urine and Meat Extracts. H. THAR (*Biochem. Zeitsch.*, 1913, **56**, 353—354).—Reply to E. Salkowski (this vol., ii, 992). S. B. S.

Urobilin and its Detection by Treating Urine with Copper Sulphate and Extraction with Chloroform. THEODOR HAUSMANN (*Chem. Zentr.*, 1913, ii, 819; from *Zeitsch. exper. Path. Ther.*, 1913, 13, 373—399).—The method depends on the fact that the urobilinogen of urine is oxidised by copper sulphate to urobilin, which may be extracted with chloroform. Twenty c.c. of the urine are mixed with 2 c.c. of 10% copper sulphate solution, and the mixture is shaken with 2 c.c. of chloroform; the chloroform layer is coloured pink, orange, or red. In the case of very acid urines the colour obtained is yellow. If, in place of copper sulphate, the urine is treated with a concentrated solution of either ferrous sulphate, zinc acetate, zinc sulphate, or potassium ferricyanide, the chloroform layer remains colourless, whilst lead acetate, mercuric chloride, and phosphotungstic acid yield precipitates with the urine, and only a small proportion of the urobilin is extracted by the chloroform; repeated extractions are necessary to obtain all the urobilin in the chloroform solution. Previous treatment of the urine with formaldehyde or dimethylaminobenzaldehyde hinders the oxidation of the urobilinogen by copper sulphate. The chloroform extract contains the actual urobilin and not its copper compound; the urobilin may be extracted from the chloroform solution by shaking the latter with sodium hydroxide solution. This alkaline solution exhibits the characteristic properties of a urobilin solution (absorption bands, fluorescence with alcoholic zinc acetate, etc.). For the estimation of the urobilin, the chloroform extract is evaporated to dryness, the residue is dissolved in $N/10$-sodium hydroxide solution, and the excess of the latter is titrated with $N/10$-hydrochloric acid; the difference between the quantities of alkali and acid solutions used is multiplied by 0·0062 to give urobilin. W. P. S.

Detection of Indoxyl in Icteric Urine. LOUIS BÉLIÈRES (*J. Pharm. Chim.*, 1913, [vii], 8, 429—430).—The presence of biliary pigments in the urine is ascertained by a preliminary test in which the urine is treated with an excess of basic lead acetate, the precipitate collected on a filter, washed with water, and then transferred to a test-tube, in which it is mixed with 20 c.c. of 9% alcohol. Hydrochloric acid is then added; the lead chloride settles rapidly, and the alcohol exhibits a green colour. The development of the coloration may be accelerated by the addition of a few drops of hydrogen peroxide solution. For the detection of indoxyl, the urine is treated with basic lead acetate, and filtered. A portion of the filtrate is mixed with an equal volume of hydrochloric acid, and shaken with chloroform; the latter exhibits the characteristic coloration. Another portion of the filtrate is treated with ammonia, the precipitate is collected on a filter, and treated with alcohol and an excess of hydrochloric acid; the alcoholic solution is coloured reddish-violet. After filtration, the solution is diluted with water and shaken with chloroform, when the latter is coloured blue, red, or violet. W. P. S.

Substances in Urine giving Rise to Indigotin. II New Qualitative Tests. ROBERT V. STANFORD (*Zeitsch. physiol. Chem.*, 1913, 88, 47—55. Compare this vol., i, 1134).—Most of the existing methods for the detection of indigotin-forming substances in urine differ only in the use of different oxidising agents, and they are all untrustworthy. The decolorisation of the indigotin solutions frequently observed is due to the presence of oxidising chloro-compounds in the chloroform used. These can be removed without difficulty, and the conditions are given for carrying out the test in the absence of air, when pure blue solutions are obtained, which can be compared colorimetrically with Fehling's solution. An alternative method is to add isatin and hydrogen chloride, and convert the indigotin compound into indirubin. When air is excluded in this case also, the method becomes more delicate, and can be applied to quantitative measurements. E. F. A.

Nephelometric Determination of Proteins: Casein, Globulin and Albumin in Milk. PHILIP A. KOBER (*J. Amer. Chem. Soc.*, 1913, 35, 1585—1593).—An improved form of nephelometer is described for the estimation of the proteins of milk by the formation of suspensoids with suitable reagents after the extraction of the fat (compare this vol., ii, 260, 355). The method, which greatly reduces the time usually necessary for such estimations, gives results which compare favourably with those of the processes at present in common use. D. F. T.

The Quantitative Estimation of Tryptophan. E. HERZFELD (*Biochem. Zeitsch.*, 1913, 56, 258—266).—The reagent used for this purpose consists of 20 grams of *p*-dimethylaminobenzaldehyde dissolved in a mixture of 500 c.c. of concentrated hydrochloric acid and 500 c.c. of water. To 50 c.c. of the solution to be tested, which contains tryptophan, are added 10 c.c. of this reagent, and the mixture is then diluted to 100 c.c. with concentrated hydrochloric acid. After thirty hours the colour is measured. (A distinct blue colour is obtained when the above mixture contains tryptophan to the extent of 1 part in 1,000,000.) The colour can be estimated approximately by comparison with an ammoniacal copper sulphate solution prepared in the following way. One gram of anhydrous copper sulphate is dissolved in 100 c.c. of water; 1 c.c. of this solution is mixed with 20 c.c. ammonia solution, and the mixture is diluted with water to 100 c.c. The colour thus obtained corresponds very nearly to that given with 0·0001 gram tryptophan with the aldehyde reagent. A more accurate way of ascertaining the amount of colour in a solution is the spectrophotometric method described in detail by the author. To estimate the tryptophan content of a protein, 1 gram of the substance is dissolved in 500 c.c. of 0·5% sodium carbonate solution, and incubated for twenty-four hours with 0·5 gram pancreatin (with known tryptophan content); 50 c.c. of the digest are then treated with the *p*-dimethyldiaminobenzaldehyde solution in the manner described above. A table is given showing the tryptophan content of various proteins. S. B. S.

CONTENTS.

PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

PAGE

INDEX OF AUTHORS' NAMES.

TRANSACTIONS, PROCEEDINGS, AND ABSTRACTS 1913.

(Marked T., P., and A., i and A., ii respectively.)

A.

B.

C.

D.

F.

G.

H.

I.

J.

K.

L.

M.

N.

P.

Q.

R.

* Formerly Berlin.

W.

INDEX OF SUBJECTS.

TRANSACTIONS, PROCEEDINGS, AND ABSTRACTS. 1913.

(Marked T., P., and A., i and A., ii respectively.)

A.

D.

E.

G.

I.

L.

M.

N.

O.

S.

U.

W.

X.

Me = 1:2 ; **m-xylene,** Me : Me = 1:3 ; **p-xylene,** Me : Me = 1:4.)

(o-*Xylene*, *Me* : *Me* = 1 :2 ; m-*xylene*, *Me* : *Me* = 1:3 ; p-*xylene*, *Me* :

INDEX TO PATENTS.

ERRATA.

Vol. XCVIII (Abstr., 1910).

Line
23 *for* "**Pinacone Transformation**" *read* "**Pinacolin Transformation.**"

Vol. C (Abstr., 1911).

10 14 *delete* "m. p. 65°."

Vol. CII (Abstr., 1912).

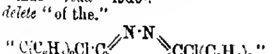
18 11* *for* "3:4-Dimethyleneoxychalkone" *read* "3:4-Methylenedioxychalkone."
18 8* ,, "3:4-*Dimethyleneoxydihydrochalkone*" read "3:4-*Methylenedioxydihydrochalkone.*"

Vol. CII (Abstr., 1912).

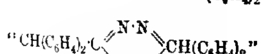
1 19 for "3-p-*dimethylaminobenzylidene-2-ketothionaphthen*" read "3-p-*dimethylaminobenzylidene-2-ketodihydrothionaphthen.*"
2 12* ,, "birefraction" *read* "birefringence."

Vol. CIV (Abstr., 1913).

2* *for* "Émile" *read* "Eugène."
1 ,, "*Pilcarpus*" read "*Pilocarpus.*"
3 ,, "pilocarpiline" *read* "carpilene."
8* ,, "**Pathology**" *read* "**Pharmacology.**"
8 ,, "benzoate (n^{18} 1·5071)" *read* "*cyclo*hexanecarboxylate."
9 ,, "*cyclo*hexanecarboxylate" ,, "benzoate (n^{18} 1·5071)."
19* } ,, "*methyl*cyclo*hexenolpyruvolactone*" read "*methyl*cyclo*hexenol-*
18* } *glyoxylolactone.*"
8 ,, "Spencer" *read* "Spence."
3 ,, "40°" *read* "46°."
8 and ii. 1182, 3* *for* "Traschennikov" *read* "Truschennikov."
8* ,, "Oppe" *read* "Oppé."
25 ,, "**Triphenylethyl**" *read* "**Triphenylmethyl.**"
11* ,, "**Relation**" *read* "**Reaction.**"
11* *Authors' names should read* "Alfred W. Bosworth and Lucius L. Van Slyke."
21* *for* "Alfons" *read* "Adolf."
10 ,, "nitric" *read* "hydrochloric."
12* ,, "ethyl" *read* "methyl."
11* ,, "borneol" *read* "bornylene" (in both instances).
11 ,, "indo-" *read* "iodo-."
17 ,, *delete* "of the."

3* ,, 

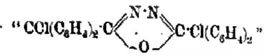
read 

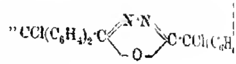
11 ,, 

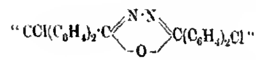
read 

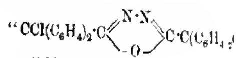
* From bottom.

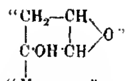
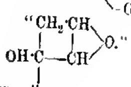
Page Line

i, 998 14* *for* "  "

read "  "

,, 2* ,, "  "

read "  "

i, 1057 14* ,, "  " *read* "  "

i, 1128 7 ,, "MENDELL" *read* "MENDEL."
i, 1128 8 ,, "WAKEMANN" ,, "WAKEMAN."
i, 1132 22* ,, "L." *read* "E."
i, 1133 19* ,, "A." ,, "E."
i, 1138 25 } 17* } ,, "GILMAN" *read* "GILMOUR."
i, 1349 12* and ii, 1208, 9* ,, "MURDROVCIC" *read* "MUDROVČIĆ."
i, 1393 6* ,, "1:3:6-*triacetyl-5-aminohydantoin*" read "5-*acetylami*… *diacetylhydantoin*."
,, 3* ,, "1:6-*diacetyl-5-aminohydantoin*" read "5-*acetylamino-1*-… *hydantoin*."
ii, 66 16* ,, "**Sardaigne**" *read* "**Sardinia**."
16* ,, "CESARO" *read* "CESÀRO."
13* } 9* } ,, "orthose" ,, "orthoclase."
ii, 353 21 ,, "**Melitolus**" *read* "**Melilotus**."
,, ,, ,, "**Officinalus**" *read* "**Officinalis**."
ii, 438 9* ,, "RIECKE" *read* "RIEKE."
ii, 474 3* ,, "ANTON" *read* "ANATOLE."
ii, 546 21* ,, "**Albumin**" *read* "**Aluminium**."
ii, 621 15* ,, "690–691" *read* "677–679, 690–691."
ii, 649 9 } 17* } ,, "HOUSTON" *read* "HOUSTOUN."
ii, 650 14 }
ii, 822 10 ,, "KAMMERLINGH" *read* "KAMERLINGH."
ii, 825 7* ,, "OSTERHELD" *read* "OESTERHELD."
ii, 857 22 ,, "GEHLOFF" *read* "GEHLHOFF."
ii, 857 23 ,, "**19**" *read* "**14**."
ii, 879 17* ,, "TORN" *read* "HORN."
ii, 991 9* ,, *after* "seven" *delete* "to" *and insert* "minutes at 115 … In using the autoclave for conversion the best results … obtained by heating for."
ii, 1076 15* ,, "ERLENMAYER" *read* "ERLENMEYER."
ii, 1098 under **Bart**, *for* "413" *read* "415."
ii, 1102 col. i. 28* *for* "**Riecke**" *read* "**Rieke**."
ii, 1141 ,, 17* ,, "**Willsdon**" *read* "**Willson**."
ii, 1172 ,, 4* ,, "**Kirpetchev**" *read* "**Kirpitchev**."
ii, 1260 col. ii. 21 ,, "**Willsdon**" *read* **Willson**."
ii, 1191 under **Mannich**, *for* "86" *read* "87."

COLLECTIVE INDEX 1903—12 (AUTHORS).

535 25 col. ii, *for* "1909" *read* "1908."

* From bottom.

͵STRUCTIONS TO ABSTRACTORS,

GIVING THE

ENCLATURE AND SYSTEM OF NOTATION

ADOPTED IN THE ABSTRACTS.

ıbject of the abstracts of chemical papers published elsewhere the Transactions of the Society is to furnish the Fellows with ·e account of the progress of chemical science from month to It must be understood that as the abstracts are prepared information of the Fellows in general, they cannot possibly be ı full or so detailed as to obviate on the part of tho·e who are ¦ on special investigations the necessity of consulting the memoirs.

ıs of papers must be given literally.

ıre beginning to write the abstract, the whole of the original st be read, ın order that a judgment may be formed of its ·e and of the scale on which the abstract should be made.

he case of papers dealing with subjects not strictly chemical, ·act should refer only to matters of chemical interest in the

abstract should consist mainly of the expression, in the ı's own words, of the substance of the paper.

ı abstract should be made as short as is consistent with a . accurate statement of the author's results.

oncise statement showing the general trend of the investigation e given at the commencement of those abstracts where the ! the original permits of it.

ın abstract of a paper on the same subject, either by the ' the paper abstracted, or by some other author, has already , note should, as a rule, be made of this fact.

tter which has appeared once in the *Abstracts* is not to be d again, a reference being given to the volume in which the may be found.

a rule, details of methods of preparation or analysis, or speaking of work, are to be omitted, unless such details are to the understanding of the results, or have some inde- value. Further, comparatively unimportant compounds, such organic salts of organic bases or acids, should be mentioned rtly. On the other hand, data such as melting and boiling p. gr., specific rotation, &c., must be given in every case unless in earlier papers.

10. Employ names such as *sodium chloride*, *potassium sulp*[h...] inorganic compounds, and use the terminals *ous* and *ic* only tinguishing compounds of different orders derived from th[e] elementary radicle; such, for instance, as mercurous and m[ercuric] chlorides, sulphurous and sulphuric acids.

11. Term compounds of metallic radicles with the OH *hydroxides* and not hydrates, the name hydrate being reserved f[or com]pounds supposed to contain water of combination or crystallisa[tion].

12. Term salts containing an amount of metal equivalent di[s]placeable hydrogen of the acid, *normal* and not neutral sal[ts] assign names such as sodium hydrogen sulphate, disodium hy[drogen] phosphate, &c., to the acid salts. Basic salts as a rule are bes[t desig]nated merely by their *formulae*.

13. Names in common use for oxides should be employ[ed] example: NO, nitric oxide; CO_2, carbon dioxide; P_4O_{10}, pho[sphoric] oxide; As_4O_6, arsenious oxide; Fe_2O_3, ferric oxide.

14. In open chain compounds, Greek letters must be used to the position of a substituent, the letter α being assigned to carbon atom in the formula, except in the case of CN and for example, $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2I$ α-iodobutane, $CH_3 \cdot CH_2 \cdot$(α-cyanopropane.

15. Isomeric open chain compounds are most convenientl[y repre]sented as substitution derivatives of the longest carbon chai[n in the] formula; for example,

$$\begin{matrix} CH_3 \\ CH_3 \cdot CH_2 \end{matrix} \!\!> CH \cdot CH <\!\! \begin{matrix} CH_3 \\ CH_3 \end{matrix} \quad \text{or} \quad CH_3 \cdot CH_2 \cdot CHMe \cdot CHMe \cdot C$$

should be termed βγ-dimethylpentane not methylethyli[sopropyl]methane, and $\begin{matrix} CH_3 \\ CH_3 \end{matrix} \!\!> CH \cdot CH <\!\! \begin{matrix} CH_3 \\ CO_2H \end{matrix}$ or $CH_3 \cdot CHMe \cdot CHM$[e...] should be termed αβ-dimethylbutyric acid, not αββ-trimethylp[ropionic] or α-methyl*iso*valeric, or methyl*iso*propylacetic acid.

16. Use names such as methane, ethane, &c., for the paraffins or hydrocarbons of the C_nH_{2n+2} series of th[e type] $CH_3 \cdot [CH_2]_5 \cdot CH_3$, &c. Term the hydrocarbons C_2H_4 and C_2H_2 [ethylene] and acetylene respectively (not ethene and ethine). Homol[ogues of] the ethylene series are to be indicated by the suffix *-ene*, and [of] the acetylene series, wherever possible, by *-inene*. Adopt th[e name] allene for the hydrocarbon $CH_2{:}C{:}CH_2$.

17. Distinguish all hydroxyl derivatives of hydrocarbons b[y names] ending in *ol*. Alcohols should be spoken of as mono-, di-, n-hydric, according to the number of OH-groups. Compoun[ds which] are not alcohols, but for which names ending in *ol* have be[en used,] are to be represented by names ending in *ole*, if a systemat[ic name] cannot be given, thus anisole not anisol, indole not indol. Co[mpounds] such as MeONa, EtONa, &c., should be termed sodium me[thoxide,] sodium ethoxide, &c.

18. The radicles indicated in the name of a compound a[re]

n the order fluoro-, chloro-, bromo-, iodo-, nitro-, nitroso-, imino-, cyano-, thiocyano-, hydroxy-, keto-.

Compounds analogous to the acids of the lactic series containing group should be termed *hydroxy*-derivatives, and not oxy-deriva- or example, hydroxyacetic and not oxyacetic acid. Compounds ing the analogous groups OEt, OPh, OAc, &c., should in like be termed ethoxy-, phenoxy-, acetoxy- derivatives. Thus ypropionic acid, OEt·CHMe·CO_2H, instead of ethyl-lactic acid; thoxybenzoic acid, $(OEt)_2C_6H_3$·CO_2H, instead of diethylproto- ic acid; and α-acetoxypropionic acid, OAc·CHMe·CO_2H, instead yl-lactic acid. Terms such as diethylprotocatechuic acid should erstood to mean a compound formed by the displacement of en atoms in the hydrocarbon radicle of protocatechuic acid by hus, $C_6HEt_2(OH)_2$·CO_2H, and not $C_6H_3(OEt)_2$·CO_2H, just as protocatechuic acid is understood to be the name of a compound ormula $C_6HBr_2(OH)_2$·CO_2H.

The term *ether* should be restricted to the oxides of hydro- radicles and their derivatives, and the esters (so-called com- thers or ethereal salts) should be represented by names similar given to metallic salts.

When a substituent is one of the groups NH_2, NHR, NR_2, NH or name should end in *ino*; for example, β-aminopropionic acid, H_2·CH_2·CO_2H, β-anilino-acrylic acid, NHPh·CH:CH·CO_2H, propionic acid, NH:CMe·CO_2H.

ompounds of the radicle SO_3H should, whenever possible, be ulphonic acids, or failing this, sulpho-compounds; for example, sulphonic acid, sulphobenzoic acid.

Basic substances should invariably be indicated by names in *ine*, as aniline instead of anilin, the termination *in* being d to certain neutral compounds, viz., glycerides, glucosides, rinciples, and proteins, such as palmitin, amygdalin, albumin. npounds of basic substances with hydrogen chloride, bromide e should always receive names ending in *ide* and not *ate*, as e hydrochloride and not morphine hydrochlorate.

he Collective Index, 4th decade (1903–1912) should be adopted tandard of reference on questions of nomenclature not provided e preceding sections.

Notation.

n empirical formulae the elements are to be given in the H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically. quations should be omitted unless essential to the under- of the results, as a rule, they should not be written on a line, but should "run on" with the text.

o economise space, it is desirable:

(a) That *dots* should be used instead of *dashes* in connecting contiguous symbols or radicles, whenever this does not interfere with the clearness of the formula.

(b) That formulae should be shortened by the ju employment of the symbols Me for CH_3, I C_2H_5, Pr$^\alpha$ for $CH_2{\cdot}CH_2{\cdot}CH_3$, Pr$^\beta$ for CH(CH for C_6H_5, Py for C_5H_4N, Ac for $CO{\cdot}CH_3$, and $CO{\cdot}C_6H_5$.

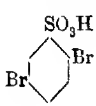
(c) That formulae should be written *in one line* wh this can be done without obscuring their meani

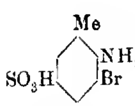
28. In representing the constitution of benzene derivativ relative positions of the radicles in the symbol of benzene sho indicated by numerals, instead of by means of the hexagon for

(a) The abbreviations *o*-, *m*-, and *p*-, should be used in of 1 : 2- or ortho-, 1 : 3- or meta-, and 1 : 4- or p

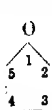
(b) In numbering positions in the case of substitution tives of phenol, aniline, benzonitrile, benzoi benzenesulphonic acid, benzaldehyde, and t the characteristic radicle of each of these substances is to be regarded as in position 1 (co Collective Index).

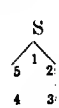
(c) Names of substitution derivatives should be gi such a way that the position of the substitu indicated by a numeral prefixed ; for example

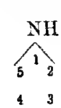

is 2 : 5-dibromobenzenesulphonic acid ;

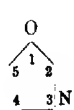

is 3-bromo-*o*-toluidine-5-sulphonic acid.

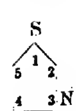
29. In representing the constitution of derivatives of other " chain" hydrocarbons, graphic formulae should not be employe the system of numbering positions indicated in Richter's *Lexil Kohlenstoff-Verbindungen* (3rd edition, 1910, pp. 14—26) sho used, of which the following schemes may be regarded as typic

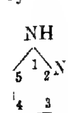

Furan.


Thiophen.


Pyrrole.

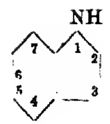

Oxazole.


Thiazole.

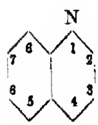

Pyrazole.

5

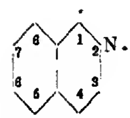
Pyridine.



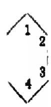
Indole.



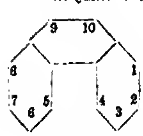
Quinoline.



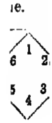
*iso*Quinoline.

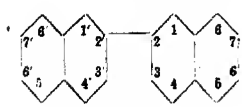


ıe.



Phenanthrene.





ββ-Dinaphthyl.

Manuscript.

difficulty of dealing with MSS. of widely varying
ıot be accepted unless written on quarto paper

ı one abstract must appear on a sheet.
ract exceeds a sheet in length, the sheets must be
means of gum at the top left-hand corner.
he abstractor must be written diagonally at the
of the first sheet of the abstract.

Proofs.

e expected to read and correct proofs carefully,
ulae and figures against MSS.
vever small, must be returned to the Sub-Editor
rs after receipt from the printers.

**decision, in all matters connected with the
considered final.**

osed originally by E. Fischer, *is adopted in the text of the*

JOURNALS FROM WHICH ABSTRACTS ARE MA

All references to Journals should give the abbreviated title, the year of pu the series, the volume and the page; thus *Ber.* 1901, **34**, 2455; *Bull. S* 1901, [iii], **25**, 794; *Gazzetta* 1901, **31**, i, 554.

ABBREVIATED TITLE.	JOURNAL.
Amer. Chem. J.	American Chemical Journal.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Physiol	American Journal of Physiology.
Amer. J. Sci.	American Journal of Science.
Anal. Fis. Quim.	Anales de la Sociedad Española Fisica y Quí
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l' à l'Agriculture, à la Pharmacie et à la B
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Ann. Falsif.	Annales des Falsifications.
Ann. Inst. Pasteur	Annales de l'Institut Pasteur.
Ann. Physik	Annalen der Physik.
Ann. sci. Univ. Jassy	Annales scientifiques de l'Université de Jas
Arch. expt. Path. Pharm.	Archiv für experimentelle Pathologie und logie.
Arch. Hygiene	Archiv für Hygiene.
Arch. Néerland.	Archives Néerlandaises des sciences exacte elles.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Sci. phys. nat.	Archives des Sciences physiques et naturel
Arkiv Kem. Min. Geol.	Arkiv för Kemi, Mineralogi och Geologi.
Atti R. Accad. Sci. Torino.	Atti della Reale Accademia delle Scienze d
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei.
Ber.	Berichte der Deutschen chemischen Gesell
Ber. Deut. bot. Ges.	Berichte der Deutschen botanischen Gesell
Ber. Deut. pharm. Ges.	Berichte der Deutschen pharmazeutischen G
Ber. Deut. physikal. Ges	Berichte der Deutschen physikalischen Ges
* *Bied. Zentr.*	Biedermann's Zentralblatt für Agrikultur rationellen Landwirtschafts-Betrieb.
Bio-Chem. J.	The Bio-Chemical Journal.
Biochem. Zeitsch.	Biochemische Zeitschrift.
Boll. chim. farm.	Bollettino chimico farmaceutico.
Bull. Acad. roy. Belg.	Académie royale de Belgique—Bulletin d des Sciences.
Bull. Acad. Sci. Cracow	Bulletin international de l'Académie des S Cracovie.
Bull. Acad. Sci., St. Pétersbourg.	Bulletin de l'Académie Impériale des Scie Pétersbourg.
Bull. Assoc. chim. Sucr. Dist.	Bulletin de l'Association des chimistes de de Distillerie.
Bull. Geol. Soc. Amer.	Bulletin of the Geological Society of Ameri
Bull. Imp. Inst.	Bulletin of the Imperial Institute.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg.	Bulletin de la Société chimique de Belgique
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralog
Bull. Soc. ind. Mulhouse	Bulletin de la Société industrielle de Mulho
Centr. Bakt. Par.	Centralblatt für Bakteriologie, Parasitenk Infektionskrankheiten.
Centr. Min.	Centralblatt für Mineralogie, Geologie und logie.
* *Chem. Zentr.*	Chemisches Zentralblatt.
Chem. News	Chemical News.
Chem. Rev. Fett-Harz-Ind.	Chemische Revue über die Fett- und Harz-I

* Abstracts from the *Zentralblatt* are made only in the case of papers journals other than those included in this list.

RNALS FROM WHICH ABSTRACTS ARE MADE.

D TITLE.	JOURNAL.
	Chemisch Weekblad.
	Chemiker Zeitung.
	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
ord	Experiment Station Record.
	Gazzetta chimica italiana.
	Geological Magazine.
	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
il.-Bd.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie. Beilage-Band.
tiv. Elektro-	Jahrbuch der Radioaktivität und Elektronik.
	Journal of Agricultural Science.
. Soc.	Journal of the American Chemical Society.
	Journal of Biological Chemistry, New York
	Journal de Chimie physique.
	Journal of Geology.
	Journal of Hygiene.
hem.	Journal of Industrial and Engineering Chemistry.
ng	Journal of the Institute of Brewing.
	Journal für Landwirtschaft.
ch	Journal of Medical Research.
	Journal of Pathology and Bacteriology.
im.	Journal de Pharmacie et de Chimie.
em.	Journal of Physical Chemistry.
	Journal of Physiology.
	Journal für praktische Chemie.
. Soc.	Journal of the Royal Agricultural Society.
New South	Journal of the Royal Society of New South Wales.
Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
Ind.	Journal of the Society of Chemical Industry.
	Journal of the Society of Dyers and Colourists.
m Acad. Sci.	Journal of the Washington Academy of Sciences.
-Akad. Handl.	Kongl. Svenska Vetenskaps-Akademiens Handlingar.
ch.	Kolloid Zeitschrift.
Beihefte	Kolloidchemische Beihefte.
	The Lancet.
uchs-Stat.	Die landwirtschaftlichen Versuchs-Stationen.
	Le Radium.
Sci. Torino	Memorie della Reale Accademia delle Scienze di Torino.
Sci. Eng. Kyōtō	Memoirs of the College of Science and Engineering, Kyōtō Imperial University.
ester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
	Metallurgie.
	Milchwirtschaftliches Zentralblatt.
	Mineralogical Magazine and Journal of the Mineralogical Society.
	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
	Il Nuovo Cimento.
	Archiv für die gesammte Physiologie des Menschen und der Thiere.
	Pharmaceutical Journal.
l	Pharmaceutisch Weekblad.
	Pharmazeutische Zeitung
	Pharmazeutische Zentralhalle.
	Philippine Journal of Science.

JOURNALS FROM WHICH ABSTRACTS ARE MADE.

ABBREVIATED TITLE.	JOURNAL.
Phil. Mag.	Philosophical Magazine (The London, Edinl Dublin).
Phil. Trans.	Philosophical Transactions of the Royal London.
Physikal. Zeitsch.	Physikalische Zeitschrift.
Proc. Amer. Physiol. Soc.	Proceedings of the American Physiological
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical
Proc. K. Akad. Wetensch. Amsterdam.	Koninklijke Akademie van Wetenschappen t dam. Proceedings (English version).
Proc. Phil. Soc. Glasgow	Proceedings of the Glasgow Philosophical So
Proc. Physiol. Soc.	Proceedings of the Physiological Society.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinbu
Quart. J. exp. Physiol.	Quarterly Journal of experimental Physiolo
Quart. J. Geol. Soc.	Quarterly Journal of the Geological Society.
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Ba Belgique.
Rend. Accad. Sci. Fis. Mat. Napoli.	Rendiconto dell' Accademia delle Scienze Matematiche-Napoli.
Rev. de Métallurgie	Revue de Métallurgie.
Sci. Proc. Roy. Dubl. Soc.	Scientific Proceedings of t Dublin
Sci. Trans. Roy. Dubl. Soc.	Scientific Transactions of al Dublin
Sitzungsber. K. Akad. Wiss. Berlin.	Sitzungsberichte der Kö reussischen der Wissenschaften in
Sitzungsber. K. Akad. München.	Sitzungsberichte der k bayerischen der Wissenschaften zu München.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemi
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Nova Scotia Inst. Sci.	Transactions of the Nova Scotia Institute o
Trans. Path. Soc.	Transactions of the Pathological Society.
Trans. Roy. Soc. Canada	Transactions of the Royal Society of Canad
Trans. Roy. Soc. Edin.	Transactions of the Royal Society of Edinb
Trans. Roy. Irish Acad.	Transactions of the Royal Irish Academy.
Tsch. Min. Mitt.	Tschermak's Mineralogische Mitteilungen.
U.S.A. Dept. Agric. Bull.	Bulletins of the Department of Agriculture,
U.S.A. Dept. Agric. Rep.	Reports of the Department of Agriculture,
Verh. Ges. deut. Naturforsch. Aerzte	Verhandlung der Gesellschaft deutscher Na und Aerzte
Wiss. Abhandl. Phys.-Tech. Reichsanstalt.	Wissenschaftliche Abhandlungen der Ph Technischen Reichsanstalt.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeitsch. Biol.	Zeitschrift für Biologie.
Zeitsch. Elektrochem.	Zeitschrift für Elektrochemie.
Zeitsch. Kryst. Min.	Zeitschrift für Krystallographie und Miner
Zeitsch. Nahr. Genussm.	Zeitschrift für Untersuchung der Nahr Genussmittel.
Zeitsch. öffentl. Chem.	Zeitschrift für öffentliche Chemie.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, St und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologisc
Zeitsch. prakt. Geol.	Zeitschrift für praktische Geologie.
Zeitsch. Ver. deut. Zuckerind.	Zeitschrift des Vereins der deutschen Zucker
Zeitsch. wiss. Photochem.	Zeitschrift für wissenschaftliche Photograp physik und Photochemie.
Zeitsch. Zuckerind. Böhm.	Zeitschrift für Zuckerindustrie in Böhmen.